











*Outlines of*  
PHYSICAL CHEMISTRY



*Outlines of*  
**PHYSICAL  
CHEMISTRY**

By the late **FREDERICK H. GETMAN**

*Seventh Edition*

By **FARRINGTON DANIELS**

**PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF WISCONSIN**

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## PREFACE

The present revision involves rearrangement, the addition of more advanced material, particularly in the first part of the book, the inclusion of new developments in physical chemistry, and a somewhat different approach to thermodynamics and to the phase rule. Mathematical operations and practical applications are emphasized with the help of frequent examples.

The author is indebted to the teachers of physical chemistry and others who have given many valuable suggestions. He desires particularly to acknowledge the ideas which he has obtained from his colleagues and former associates, D. W. Osborne, W. E. Roseveare, R. H. Gillette, J. O. Hirschfelder, J. W. Williams, T. F. Anderson, C. H. Sorum, A. E. Edwards, E. G. Foster, T. P. Kohman, T. Higuchi, and C. W. Lines, and to express his appreciation for the suggestions from H. S. Van Klooster, R. T. Birge, K. Fajans, G. K. Rollefson, G. W. Wheland, H. B. Friedman, E. L. Henderson, V. Sivertz, L. J. Bircher, and many others. He wishes also to thank H. H. Schmalz for help in preparing the drawings, and J. F. Mortimer, W. G. Hendrickson, R. O. Wilfong, R. A. Buckley, and C. A. Boyd for help in checking problems and proof.

FARRINGTON DANIELS

MADISON, WISCONSIN  
*September, 1941*





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### Table of Important Constants

The following approximate values will be used for problems. Most of them are sufficiently important to memorize during the course of the work.

Acceleration of gravity	980.7
Molar volume (0°, 1 atm.) (liters)	22.41
Ice point (0°)	273.1°
One calorie (defined) (joules)	4.183
$R$ (joules)	8.314
$R$ (calorie)	1.987
$R$ (liter-atmosphere)	0.08205
Faraday (coulombs)	96,500
Avogadro number	$6.02 \times 10^{23}$
Planck's constant	$6.62 \times 10^{-27}$
Velocity of light (cm.)	$3 \times 10^{10}$
Conversion $\log_{10}$ to $\log_e$	2.303

These and other constants are given with the highest precision now warranted, on page 657.

## CHAPTER I

### FUNDAMENTAL CONCEPTS

**Physical Chemistry.** The purpose of the study of physical or theoretical chemistry is to understand and use the laws of chemistry and physics.

The first attempt to summarize the more important facts and ideas of chemistry was made in 1808 by Dalton in his "New System of Chemical Philosophy." Developments in physics and thermodynamics were next systematized, but they were not absorbed into physical chemistry until much later. In fact, physical chemistry was first considered a separate branch of science about half a century ago. It has continually broadened its scope with new discoveries and has become more exact with improvement in experimental measurements and greater use of mathematics. The boundaries of physical chemistry are not sharp; they overlap physics on the one side and all branches of chemistry on the other. As physical chemistry draws its facts from all these fields of knowledge, it in turn aids them by correlating these facts.

This correlation of phenomena may be expressed by means of word descriptions, graphical representations, or mathematical formulas. Pictures and mechanical analogies are sometimes helpful, but they must be unhesitatingly discarded if they do not promote comprehension. One of the greatest helps to the quantitative description of chemical facts lies in describing the phenomenon in terms of energy, for energy can be easily measured and described.

**Scientific Method.** Chemistry and all other sciences are based upon experimentally established facts. When a number of facts have been collected and classified, we may draw inferences as to the probable behavior of systems under conditions which have not been investigated. This process of reasoning we term generalization, and the conclusion we call a *law*. The law is not necessarily an expression of infallible truth but is rather a condensed statement of facts which have been discovered by experiment. It enables us to predict results without continued recourse to experiment.

Natural laws may be discovered either by the correlation of experimentally determined facts, as outlined above, or by means of a



speculation as to the probable cause of the phenomenon in question. Such a speculation regarding the cause of a phenomenon is called an *hypothesis*. After an hypothesis has been subjected to the test of experiment and has been shown to apply to a large number of phenomena it is termed a *theory*.

Usually science progresses by inductive reasoning from a few facts, followed by deductive reasoning based on the hypotheses, and then tested by experimental measurements designed to prove or disprove the theoretical deduction. Ingenuity in designing test experiments to check these hypotheses has been responsible in large part for the rapid progress which has been made in the natural sciences.

Most hypotheses are destined to be discarded when new facts and more precise data are obtained, but they fulfil a very necessary function in the development of science. They may be likened to the scaffolding which is used temporarily during the construction of a permanent building. A successful hypothesis is not necessarily a permanent hypothesis, but it is one which stimulates additional research, opens up new fields or explains and coordinates previously unrelated facts. The scientist needs imagination in creating new hypotheses no less than he needs ingenuity and skill in devising experiments to test them.

One of the greatest helps in the development of hypotheses and in the practical application of theoretical chemistry is mathematics. In recent years there has been a decided trend toward more extensive use of mathematics in chemistry, and the chemist has seen several of his own problems solved by physicists and mathematicians who have been led to successful hypotheses through their ability to express the experimental facts in precise mathematical terms.

**Atoms.** Natural phenomena in chemistry and physics are concerned with matter at rest or in motion, with electricity, or with radiation.

Considerable progress has been made in visualizing the corresponding units—the atom of matter, the electron of electricity, and the quantum of radiation.

Until the present century it was thought that atoms were the ultimate units of the elements, units which could not be resolved into smaller particles; but it is now well established that atoms are composed of very dense, positively charged nuclei surrounded by small units of negative electricity called electrons. These dense nuclei of the atoms have been explored with amazing success during the past decade, and we know that they in turn are composed of smaller units. Of the light units the positively charged are called positrons and the

negatively charged are called electrons, whereas of the heavier units, the neutral ones are called neutrons and the positively charged ones are called protons. Mesotrons are larger fragments obtained from nuclei.

Disintegration of atomic nuclei into these units together with nuclei of lower atomic weight has been accomplished by bombardment with particles expelled from radioactive elements or driven by high voltages. These changes involve transmutation of the elements.

In spite of the discovery of smaller subunits of the atoms, the concept of atoms and molecules remains still the background of all chemistry. Although the atoms can be disintegrated under special conditions of enormous energy, they pass unchanged through all ordinary chemical reactions and physical changes.

An hypothesis of atoms was known from the times of the Greek philosophers, but it could not be developed until quantitative experimental facts became available. Late in the seventeenth century Boyle seems to have looked upon chemical combination as the result of atomic association. Guided by these early speculations and influenced by the writings of Sir Isaac Newton, Dalton formed a mental picture of the part played by atoms in the act of chemical combination. According to his atomic theory, matter is composed of extremely minute, indivisible particles or atoms. All atoms of the same element are of equal weight, but atoms of different elements have weights proportional to their combining ratios. Chemical compounds are formed by the union of atoms of different kinds. In this way a simple, rational explanation is offered for the empirical laws of chemical combination which are known to every student of elementary chemistry.

It remained for the Italian physicist, Avogadro, in 1811, to point out the distinction between atoms and molecules. He defined the atom as the smallest particle which can enter into chemical combination, whereas the molecule is the smallest portion of matter which can exist in a free state. He then formulated the following hypothesis: "Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules." This hypothesis has been important in the development of chemistry.

**Atomic Weights.** Before the relation between atomic weights and molecular weights could be fully appreciated, it was necessary to collect a large amount of experimental data on combining weights of elements in different compounds and to discover certain guiding principles. Dulong and Petit in 1819 pointed out that for most elements the product of the specific heat and the atomic weight is approxi-

mately 6.4, so the atomic weight of an element can be estimated by dividing this constant by the specific heat of the element. The difference between atomic and molecular weights was pointed out clearly by Cannizzaro in 1858.

The powerful stimulus of hypotheses in furthering careful experimental work is well illustrated in this field. Shortly after the announcement of Dalton's atomic theory Berzelius set out to obtain the first table of atomic weights. A little later, in 1815, Prout suggested that the atomic weights of the elements are exact multiples of the atomic weight of hydrogen. To test the accuracy of this hypothesis, Stas undertook the redetermination of the atomic weights of several elements with a high degree of accuracy. This important series of investigations disproved Prout's hypothesis as originally stated. Now, more than a century later, we know that Prout's hypothesis is essentially correct and that the deviations from whole numbers are due largely to the existence of isotopes which have the same chemical properties but different atomic weights.

Again, the periodic table of Mendeleeff in 1869 led to renewed experimental activity. When the elements were arranged in the order of their atomic weights, several of them fell into groups with which their chemical and physical properties did not correspond; Mendeleeff asserted that the commonly accepted atomic weights of these elements were erroneous. A careful redetermination of atomic weights followed, and many of his predictions were confirmed. Finally, the developments in the theory of radioactive disintegration led Richards in 1913 to make a careful study of the atomic weights of elements from radioactive minerals; it was found that lead from different radioactive minerals has different atomic weights, thus fully establishing the theory of isotopes.

Great care has been expended in determining, by chemical means, the exact atomic weights of the elements. In this work of purification and exact analysis T. W. Richards and his associates have been most prominent. The latest values of the atomic weights accepted by the International Union of Chemistry for 1941 are given in the appendix on page 672. The atomic weights are of the utmost importance in practical chemistry, but their theoretical significance is less important than was formerly believed. Nearly all the chemically determined atomic weights are the averages of the weights of two or more isotopes, and but little progress has been made in predicting the distribution ratios of these isotopes. As a matter of fact, the masses of these isotopes can be more accurately determined by physical means than the average atomic weights can be determined by chemical means.

The practical limits of accuracy in atomic-weight measurements of the lightest elements have probably been reached, for the isotope ratio may vary by as much as one part in ten thousand or in one hundred thousand, depending upon the previous history of the sample and the exchange of isotopes involved in the purification and preparation of the material for analysis.

**The Avogadro Number.** The number of molecules in a gram-molecule,  $6.02 \times 10^{23}$ , has been called the Avogadro number; it is a fundamental constant in physical chemistry.

The value of this constant has been determined in many different ways which are entirely independent of each other, and the agreement is remarkably good. Perrin determined the constant from observations of Brownian motion; Rutherford, from a determination of the charge on the alpha particle from radium; Boltwood and Curie, by direct counting of alpha particles and by measurement of the volume of helium resulting from them; and Planck, from an experimental determination of the constants of radiation.

One of the most accurate values is based on Millikan's classical oil-drop experiment in which the charge on the electron was determined. The best value at present is  $6.023 \times 10^{23}$ \* and is obtained from studies of crystals with x rays whose wavelengths have been determined by diffraction from ruled gratings.

The weight of a single atom or molecule is obtained by dividing the respective atomic or molecular weight by the Avogadro number. For example, the weight of an atom of hydrogen is  $1.008/6.02 \times 10^{23} = 1.67 \times 10^{-24}$  gram; and the weight of a molecule of hydrogen chloride is  $36.46/6.02 \times 10^{23} = 6.06 \times 10^{-23}$  gram.

The Avogadro number is so very large that it can hardly be visualized. Very few operations or analytical tests in chemistry can be carried out with less than a millionth of a gram-molecule, and even a millionth of a gram-molecule contains six hundred thousand million million molecules.

**Electrons.** Electrons have a charge of  $1.60 \times 10^{-19}$ † coulomb. When an electrical field is applied they can travel along a metal wire or across an evacuated tube. When electrons move they generate a magnetic field and can turn the armature of an electric motor. When they pass through a wire of high resistance they generate heat; if the wire is heated to a high temperature, part of the energy is given out in the form of radiation as in the ordinary electric-light bulb. When

\* This value, together with the best values of other fundamental constants, is given on page 657.

† A more precise value is given in the appendix on page 657.

electrons are removed from atoms, positive ions are produced; and when extra electrons are attached to atoms, negative ions are produced.

During electrolysis electrons are supplied at the cathode and removed at the anode; and, in general, chemical reduction corresponds to the addition of electrons and oxidation to the removal of electrons.

When ions collide with a metallic electrode there may be a transfer of electrons between the two, giving to the electrode a positive or a negative charge. The potential of the electrode provides an exact method for measuring the effective concentrations of ions. The measurement of hydrogen-ion concentration with a hydrogen electrode in this way is of considerable practical importance.

The concept of electrons is particularly important in our present view of the structure of atoms and molecules.

**Electrons in Atoms.** The number of negative electrons surrounding the dense positive nucleus of an atom is called the *atomic number*. It can be determined experimentally in an unknown element by measuring the frequency of x rays which are emitted. The lightest atom, hydrogen, has one electron and the heaviest atom, uranium, has ninety-two. Their atomic numbers are 1 and 92. All the other elements have atomic numbers between these. These electrons are arranged in shells around the central nucleus of an atom, the number in each shell being limited by the rules of the quantum theory discussed on page 638. The maximum number of electrons in the first shell is two; the maximum in the second shell is eight; and larger encircling shells are limited to eighteen and thirty-two. Attempts have been made to visualize these shells of electrons as cubes with eight corners; or as a series of elliptical orbits in which the electrons travel. However, these pictures are incomplete and unnecessary. The limitations of the number of electrons in a given shell lead to the familiar periodic table of the elements given in Table I, where the atomic numbers are shown in heavy type and the atomic weight (as determined chemically) in light type. The atomic number of an element determines its position in the periodic table and this position in turn determines its chemical properties.

Hydrogen has one extranuclear electron, and helium has two. The first group can include only two electrons, and so lithium with three electrons has to start a new shell with its extra electron. Beryllium with an atomic number of 4 has four electrons, two of which are used in filling the first shell and two of which go into the second shell. Boron has three in the second shell; and carbon four, etc. The second shell may have eight electrons. The third reaches provisional comple-

TABLE I  
 PERIODIC TABLE

Shell	I	II	III	IV	V	VI	VII	VIII			0
1	1 H 1.0080										2 He 4.003
2	3 Li 6.940	4 Be 9.02	5 B 10.82	6 C 12.010	7 N 14.008	8 O 16.000	9 F 19.00				10 Ne 20.183
3	11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06	15 P 30.98	16 S 32.06	17 Cl 35.457				18 Ar 39.944
4	19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69	
	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916				36 Kr 83.7
5	37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc ...	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	
	47 Ag 107.880	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92				54 Xe 131.3
6	55 Cs 132.91	56 Ba 137.36	57-71 Rare Earths	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23	
	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po 210	85 At ...				86 Rn 222
7	87 Fr ..	88 Ra 226.05	89 Ac ..	90 Th 232.12	91 Pa 231	92 U 238.07	93 Np ...	94 Pu ..			

<sup>1</sup> The rare earths include the following elements: 57 La, 138.92; 58 Ce 140.13; 59 Pr, 140.92; 60 Nd, 144.27; 61 . . .; 62 Sm, 150.43; 63 Eu, 152.0; 64 Gd, 156.9; 65 Tb, 159.2; 66 Dy, 162.46; 67 Ho, 164.94; 68 Er, 167.2; 69 Tm, 169.4; 70 Yb, 173.04; 71 Lu, 174.99.

tion with eight, but in heavier elements expands to include eighteen. The properties of the elements in the third and fourth period are the expression of these relationships. Neon with an atomic number 10 has the two positions in the first shell and all eight positions in the second shell occupied. Its outermost shell is complete; and the next element, sodium, with an atomic number 11, has to start a third shell with one electron. Magnesium with an atomic number 12 has two electrons in the first shell, eight electrons in the second and two in the third shell. Chlorine has two in the first, eight in the second, and seven in the third. In argon, with an atomic number 18, the third shell is provisionally completed. Potassium with an atomic number 19 starts the fourth shell with one electron, having the inner shells filled successively with two, eight, and eight electrons. Calcium has two

electrons in the outer shell. With scandium, the number of fourth shell electrons remains two, while the third valence electron begins the expansion of the third group from eight to eighteen.

The number of loose electrons determines the valence and many chemical properties. Helium, neon, and argon are all alike in having a completed group of two or eight in their outermost shells, and all are chemically inert. The similar alkali metals, lithium, sodium, and potassium, are alike in having one electron in the outermost shell. Beryllium, magnesium, and calcium have two electrons in the outermost shell, whereas fluorine and chlorine have seven electrons in the outermost shell. The grouping of like elements in the periodic table is thus traced to the similarity in electron arrangement.

Only a few of the many interesting things concerning this arrangement of the elements can be mentioned here. The rare gases with completed shells are stable. Elements with only one electron in the outermost shell may lose that electron and tend to simulate the rare gas of next lower atomic number, whereas elements with nearly complete rare-gas configurations tend to attach more electrons and simulate the rare gas next higher in atomic number. The former elements have metallic properties, whereas the latter elements have non-metallic properties. In sodium, where there is no tendency for the atoms to gain electrons, electrical conductance is good; but in sulfur, where an atom may tend to complete its quota of eight electrons by attaching two more to complete its shell, electrons cannot migrate and the electrical conductance is very slight.

In the long periods inner groups are being reconstructed and completed. There are several different possible electronic arrangements of nearly equal energy for each atom; hence the positive valence is variable. Moreover, the ions are colored when the possible electron displacements involve energy differences so small that they correspond to visible light. The special magnetic character of the ions is due to the presence of electrons in incomplete inner shells. The rare earths, the elements between titanium and copper, and the corresponding elements in the later periods show these properties. Where the atoms have the same number of valence electrons and are of nearly the same size (rare-earth group), all the properties are very much alike.

The rare gases are the key elements in the periodic table, for they represent the completion of a shell.

**Electrons in Molecules.** The forces that hold atoms together in organic molecules and in substances like nitrogen and hydrogen differ from those which are found in inorganic compounds and in electrolytic

solutions. The distinctions between these two different types, the *nonpolar* and the *polar* compounds, will be stressed many times. The polar compounds involve chiefly the electrostatic forces, giving rise to *heteropolar bonds* or ionic linkages. The nonpolar or *homopolar bonds* involve an "exchange energy" understandable only on the basis of quantum mechanics. It is not to be thought, however, that atoms are held together exclusively by one type of bond or the other. In most linkages between atoms both electrostatic attraction and exchange energy binding are operating. There are all gradations between linkages that are predominantly homopolar and those that are predominantly heteropolar, so that complete quantitative treatment is not yet possible.

These two different types of binding were correlated and the concept of valence was amplified by the hypothesis of the electron pair proposed by G. N. Lewis.\* According to this hypothesis there is a definite tendency for electrons within a molecule to go together in pairs. This hypothesis is in agreement with the restrictions of the quantum theory, as shown on page 560.

Another rule for the arrangement of electrons within a molecule, the octet hypothesis, has been proposed by Lewis, by Kossel, and by Langmuir.† According to it, there is a tendency for eight electrons to group around each atom in a molecule. There are exceptions, and they make this rule less significant than the rule of the electron pair.

These hypotheses may be illustrated with lithium fluoride. Lithium has one electron in its outermost shell and fluorine has seven. The lithium atom tends to lose its one valence electron in the outermost shell, becoming a lithium ion with one positive charge, and the fluorine atom tends to gain an extra electron, becoming a fluoride ion with one negative charge. Both tendencies are satisfied by a transfer of an electron from the lithium to the fluorine. This electrostatic or ionic type of linkage can be broken apart by dissolving the compound in certain solvents. Lithium fluoride, for example, separates almost completely into lithium ions and fluoride ions when dissolved in water. The energy required to pull these ions apart is offset by the energy released when the ions combine with the solvent.

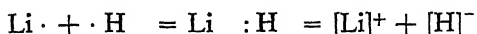
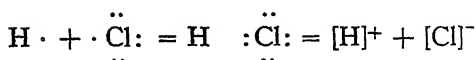
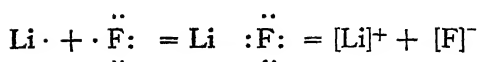
Other examples are given by the following equations, in which the numbers of electrons in the outermost shell are indicated with dots.

\* Lewis, *J. Am. Chem. Soc.*, **38**, 762 (1916); *J. Chem. Phys.*, **1**, 17 (1933); "Valence and the Structure of the Atom," Chemical Catalog Co., New York, 1923.

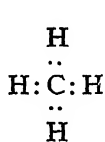
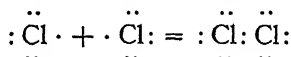
† Langmuir, *J. Am. Chem. Soc.*, **41**, 868, 1543 (1919).



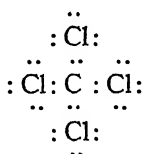
Thus:



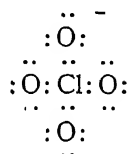
A covalent bond or homopolar bond is the same as the valence bond of organic chemistry, but it may be represented with two dots for the electron pair instead of with the straight line which is ordinarily used. The following equations and compounds illustrate the *covalent bond*:



Methane



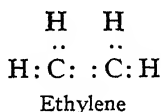
Carbon tetrachloride



Perchlorate ion

It is interesting to note that these views of valence account satisfactorily for the fact that a hydrogen atom will combine with another atom of negative chlorine or positive lithium or with another atom of hydrogen.

Double bonds and triple bonds can be represented by the sharing of two pairs or three pairs of electrons, as shown by ethylene and acetylene.



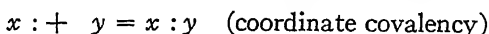
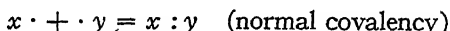
Ethylene



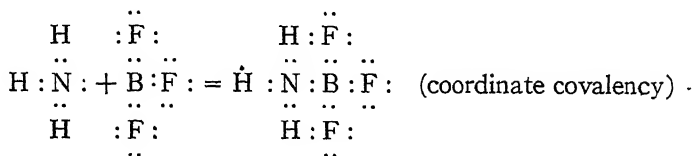
Acetylene

The possibility of these bonds is a great aid in giving variety and complexity to organic substances.

There is a special type of covalent bond, called a *coordinate covalent bond*, in which both electrons of the electron pair are contributed by the same atom, thus:



This type of linkage is recognized among organic and inorganic molecules as giving rise to special properties. An example is given among the boron compounds



As will be indicated on page 645, the electron theory of valence has been extended and applied successfully to many of the phenomena of organic chemistry.

**Binding Forces.** Atoms are held together in molecules by homopolar or heteropolar bonds as just explained, but there are other forces which hold molecules together in larger units which are sometimes called "complexes" or "associated molecules." Additional concepts of electrostatic attraction are needed to explain the formation of these other compounds.

Neutral molecules which contain unsymmetrically arranged electrical charges are called dipoles. The molecules, although neutral, have a positive and a negative part so that they can turn in such a way as to attract each other. The liquefaction of some gases and the deviation from ideal behavior in liquids and liquid mixtures can be traced to this *dipole-dipole* attraction.

Another type of electrostatic attraction is due to *induced dipoles*. Although a symmetrical molecule is neutral and balanced with reference to its electrical charges, it can by virtue of its electrical nature induce an electrical field in a neighboring molecule. The liquefaction of noble gases like argon or helium is entirely due to this induced-dipole effect. In all other cases it is responsible for part of the attractive force.

There are many different combinations of these electrostatic attractions. For example, the hydration of ions in solution or the production of complex ions is due to the *ion-dipole* interaction. A more extended treatment of these different forces will be given later on page 648. It is difficult to determine the fraction of the binding force which is to be attributed to any one type of attraction.

The *hydrogen bond* is a term applied to a type of attraction which exists between two groups which contain a hydrogen atom in special structural arrangements (page 647). It is useful in correlating the properties of a number of compounds and solutions.

**Quanta.** Just as matter consists of an aggregate of atoms and electricity is composed of electrons, so light, or any form of radiant energy, consists of small units of energy called quanta or photons. The energy,  $\epsilon$ , in one of these quanta varies with the frequency,  $\nu$ , in a manner given by the fundamental equation

$$\epsilon = h\nu$$

where  $h$  is the universal Planck constant, having a value of  $6.62 \times 10^{-27}$  erg-second. This equation is useful in the study of spectroscopy and photochemistry and in a number of physical and chemical phenomena. It is the basis of the quantum theory which has revolutionized physics and is now leading to new advances in chemistry.

When photons of light are absorbed by molecules their energy is used to displace electrons or atoms within the molecule. Again, radiation is emitted when electrons or atoms return to their normal positions in the molecule after having been displaced by the absorption of energy. They may be displaced by collisions with other molecules at high temperatures, or bombardment by electrons or ions in an electrical field, or by the absorption of light. Certain restrictions are imposed by nature in the transfer of energy within molecules, and they are now understood in terms of the quantum theory.

**Energy.** Practically all the changes studied in chemistry and physics involve a change in energy. Since energy can be measured quantitatively and easily, it constitutes an excellent means for describing and predicting the phenomena of physical chemistry. Part of the energy can be made to do useful work and part of it cannot. The available work is of fundamental importance in physical chemistry. Thermodynamics comprises a study of the relations between work, heat, and chemical change.

Ergs are the fundamental units of energy and they depend on the centimeter, the gram, and the second. The first of these is defined in terms of a standard meter bar and the second in terms of a standard kilogram weight; both are standards kept in government laboratories. The third quantity is defined by means of astronomical observations. As far as is possible in scientific work, measurements are expressed in terms of centimeters, grams, and seconds, and their derived units, i.e., in the c.g.s. system.

**Survey of Physical Chemistry.** It will be helpful for the student who is starting the study of physical chemistry to glance over the table of contents of this book.

First comes a description of the physical properties of gases and

crystals. The kinetic theory has been a great help in understanding the behavior of gases. The application of x-ray measurements has given a clear picture of the nature of solids.

Many physical properties may be predicted from the known structure of the molecules; and conversely, the arrangement of atoms within the molecule can often be determined from the measurements of physical chemistry. Because of the prevalence among organic compounds of rigid bonds rather than the more mobile electrical attractions, this discussion is confined chiefly to the field of organic chemistry.

Quantitative energy relations are introduced in the fifth chapter and run through much of the material of the remainder of the book. This chapter involves the familiar concepts of work, heat, and heat capacity. It is followed by a presentation of thermochemistry and then by the more abstract concepts of thermodynamics. The more practical applications in chemical thermodynamics are presented later because they can be understood only after the student has covered other material in the book.

The theory and properties of liquids are taken up next.

A notable part of physical chemistry is devoted to the properties of solutions. Ideal solutions which follow simple laws are discussed first and then solutions of non-volatile materials. Such properties as freezing-point depression, boiling-point elevation, and osmotic pressure are related directly to the lowering of vapor pressure. Non-ideal solutions and particularly solutions of ions require special treatment.

When a material is subdivided into exceedingly small units (but larger than molecules) and spread through a liquid or other medium, the surface area is increased enormously and the electrical charges and the combination with solvent then become dominating factors and introduce new phenomena which may be of considerable importance. These relations are discussed under colloid chemistry.

The question as to how far a chemical reaction will go and what percentage of the initial material will be converted into the final products under various conditions is studied quantitatively in the formulation of equilibrium constants.

The presentation of relations between different phases in equilibrium is illustrated with typical diagrams. The phase rule of Willard Gibbs plays an important part in their interpretation.

Although the problem of how far a reaction will go has been largely solved through thermodynamics, little is known about how fast it will go. This subject is taken up in chemical kinetics. The various ex-

pressions for reaction rates, and the mechanisms proposed to account for the reactions are discussed.

Much of the latter part of the book is devoted to relations between electricity and chemistry. It deals first with electrical conductivity and with changes occurring at the electrodes when a current is passed through the cell. Then the electromotive force of cells is studied both from a theoretical and a practical standpoint. Finally, the chemical behavior of electrolytes is considered.

Molecules usually must be activated by the addition of energy before they can react chemically. One of the simplest ways in which they become activated is through the absorption of light, and the study of photochemistry is important not only of itself but also on account of the information which it gives about the mechanism of chemical reactions.

A brief introduction to the quantum theory is necessary not only for the study of photochemistry but also for the study of many branches of modern chemistry.

Rapid developments have occurred in our knowledge of the structure of the atom, particularly with respect to the nucleus. These are discussed in the last part of the book, together with the application of the quantum theory to the periodic table and to the problem of valence.

Usually, descriptive material in each subject is followed by mathematical correlations and specific numerical examples. When possible the phenomena are described quantitatively in terms of energy changes.

## CHAPTER II

### GASES

**The Gas Laws.** Matter in the gaseous state possesses the property of filling completely and to a uniform density any available space. Among the most pronounced characteristics of gases are lack of definite shape or volume, low density, and slight viscosity. The laws expressing the behavior of gases under different conditions are relatively simple and, to a large extent, are independent of the nature of the gas. The temperature and pressure coefficients of expansion of all gases are very nearly the same, at ordinary pressures.

In 1662, Robert Boyle measured carefully the volume of gas under different pressures and found that at low pressures the volume is large and that at high pressures it is small. This led to the discovery of the familiar law that, at constant temperature, the volume of a gas is inversely proportional to the pressure. This may be expressed mathematically as follows:

$$v \propto \frac{1}{p} \quad (\text{temperature constant}) \quad [1]$$

where  $v$  is the volume and  $p$  is the pressure.

This important relation between pressure and volume of a gas is shown graphically in Fig. 1. This curve is a special case of a hyperbola, sometimes called a reciprocal curve.

In 1801, Gay-Lussac and Charles independently discovered the law of the variation of the volume of a gas with temperature. Interpreted in modern terms this law states that at constant pressure, the volume of a gas is directly proportional to its absolute temperature, or

$$v \propto T^* \quad (\text{pressure constant}) \quad [2]$$

\*  $T$  is used for absolute temperature;  $t$  for temperature on the centigrade scale.

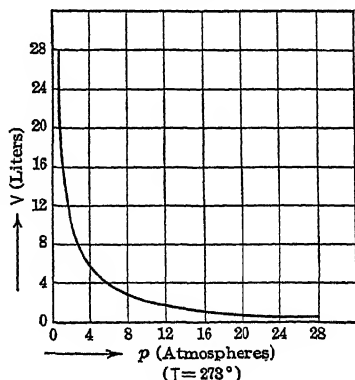


FIG. 1

This relation is shown in Fig. 2, where the direct proportionality necessarily gives a straight line.

If the volume is kept constant when the temperature is increased, the pressure increases as shown in Fig. 3. Then, at constant volume,

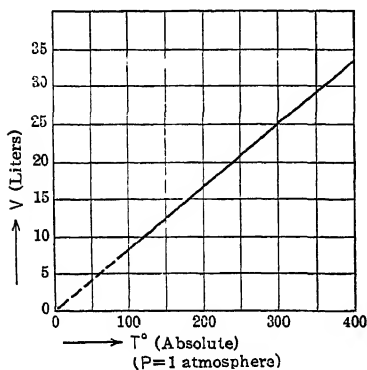


FIG. 2

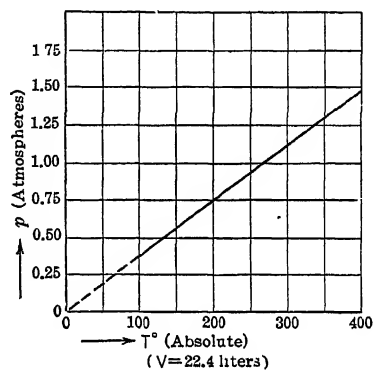


FIG. 3

the pressure of a gas is directly proportional to its absolute temperature, or

$$p \propto T \quad (\text{volume constant}) \quad [3]$$

The expressions (1) and (2) may be combined to give (4)

$$v \propto \frac{T}{p} \quad [4]$$

and introducing a proportionality factor

$$v = a \frac{T}{p} \quad [5]$$

If the equation is applied to one mole of gas (i.e., the molecular weight of the gas taken in grams), the molar gas constant,  $R$ , may be used in place of the constant  $a$  and  $V$  is used in place of  $v$ . The equation is made more general by introducing the factor  $n$ , which represents the number of moles taken.

The common expression for the simple gas laws then is

$$pv = nRT \quad [6]$$

and when  $n = 1$ ,  $pV = RT$ .

This expression is in agreement with Avogadro's law, according to

which equal volumes of gases at the same temperature and pressure contain the same number of moles.

**Evaluation of the Molar Gas Constant.** It will be remembered that a force multiplied by distance represents work, and since the product  $pV^*$  represents work, the gas constant  $R$  must be expressed in energy units divided by temperature. The numerical value may be obtained from experimental measurements; for example, it has been found experimentally that 1 mole of a perfect gas occupies 22.414 liters at  $0^\circ\text{C.}$  or  $273.16^\circ\text{K.}$ † Then

$$R = \frac{pV}{T} = \frac{1 \text{ atm.} \times 22.414 \text{ liters}}{273.16 \text{ deg.}} \\ = 0.08205 \text{ liter-atm. per degree per mole} \quad [7]$$

Obviously also using milliliters

$$R = \frac{1 \text{ atm.} \times 22,414 \text{ ml.}}{273.16 \text{ deg.}} \\ = 82.05 \text{ ml.-atm. degree}^{-1} \text{ mole}^{-1} \quad [8]$$

The liter-atmosphere or the milliliter-atmosphere is a unit of work just as is the joule or the calorie.

The pressure may be changed to dynes per square centimeter by multiplying the barometer height, 76 cm. of mercury, by the density of mercury, 13.595 at  $0^\circ$ , and the acceleration of gravity, 980.7 cm. per sec. per sec. The pressure in dynes per square centimeter multiplied by the volume in milliliters gives the work in ergs. Ergs in turn are converted into joules by dividing by  $10^7$ .

$$R = \frac{pV}{T} = \frac{76.00 \times 13.595 \times 980.7 \times 22,414}{273.16 \times 10^7} \\ = 8.314 \text{ joules degree}^{-1} \text{ mole}^{-1} \\ = 8.314 \times 10^7 \text{ ergs degree}^{-1} \text{ mole}^{-1} \quad [9]$$

Joules may be changed into calories by dividing by the conversion factor 4.183.

$$R = \frac{8.314}{4.183} = 1.987 \text{ calories degree}^{-1} \text{ mole}^{-1} \quad [10]$$

In calculations involving the gas laws it is usually convenient to express  $R$  in liter-atmospheres or in milliliter-atmospheres; in electro-

\*  $V$  may be considered as an increase in volume from zero volume.

† C. = centigrade scale; K. = absolute temperature scale. If the scale is not specified, the centigrade scale is understood.



chemical problems involving volts and coulombs,  $R$  is best expressed in joules; and in thermochemical and thermodynamical problems,  $R$  usually is given in calories. It is necessary to be thoroughly familiar with the different constants and to know which units to use in a specified problem and how to convert one into another.

**Gas Density and Molecular Weight.** Oxygen is given an atomic weight of 16 as an arbitrary standard in determining the atomic weights of other elements. Since oxygen is diatomic, 32 is taken as the molecular weight of oxygen. It has been found that at  $0^\circ \text{C.}$  and 760 mm. pressure, 32 g. of oxygen occupies a volume of 22.414 liters, after correcting for the deviations from the perfect gas laws. To determine the molecular weight of a perfect gas, then, it is only necessary to find the weight of 22.414 liters of the gas at  $0^\circ$  and 760 mm. pressure, since by Avogadro's law equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules. The *density of a gas* is the weight of one liter of the gas. Sometimes the density of a gas is expressed in terms of the ratio of the density to the density of some standard gas such as air or hydrogen.

It is inconvenient to weigh a mole of gas under standard conditions of temperature and pressure; but by means of the gas laws the determination, made at any temperature and under any ordinary pressure, can be reduced to standard conditions.

For example, if  $g$  grams of a gas is found to occupy  $v$  liters at  $T^\circ$  and  $p$  millimeters pressure, and the molecular weight  $M$  in grams occupies 22.414 liters at 760 mm. and  $273.16^\circ \text{K.}$  ( $0^\circ \text{C.}$ ), then  $g$  and  $M$  are related by the equation

$$\frac{g}{M} = \frac{pv/T}{760.0 \times 22.414/273.16} = \frac{pv \times 273.16}{760 \times 22.414T}$$

A better way of solving gas problems of this type is to use equations (6) and (7) and substitute  $g/M$  for the number of moles,  $n$ , giving

$$pv = \frac{g}{M} RT = \frac{g}{M} 0.08205T \quad [11]$$

In using this equation it is necessary to convert pressures to atmospheres ( $p$  in atmospheres =  $p$  in millimeters/760) and volumes to liters, because the gas constant  $R$  is given in liter-atmospheres. In physical chemical calculations it is always necessary to make sure that the quantities are expressed in correct units. With this formula any one of the quantities, pressure, volume, temperature, weight, or molecular weight of the gas can be calculated easily when all the others are known.

*Example 1.* Calculate the volume occupied by 50.0 g. of chlorine at 100.0° and 730 mm. pressure, assuming that the perfect gas law applies.

$$v = \frac{g}{pM} RT = \frac{50.00}{(730/760)70.91} \times 0.08205 \times 373.1 = 22.47 \text{ liters}$$

In the *Regnault method* for determining the molecular weight of a gas, a glass bulb is weighed when completely evacuated and again when filled with the gas. The volume is obtained by weighing it when filled with water. A second bulb of the same size is used as a counterpoise to avoid troublesome corrections for air buoyancy and moisture. Exact weighing of large bulbs is difficult.

The work of Baxter and Starkweather\* is a classic example of the use of this method. These authors weighed five samples of gas in two different 2-liter globes with an average reproducibility of  $3 \times 10^{-5}$  of the weight of the gas content.

The *Victor Meyer method* is convenient for the approximate determination of molecular weights of substances that can be weighed in the liquid state, thus avoiding the weighing of large vessels. A weighed quantity of liquid in a glass bulblet is evaporated in a tube heated to a constant temperature. An equivalent volume of air is driven out and measured with a gas buret at known pressure and temperature.

*Example 2.* Calculate the molecular weight of ethyl bromide from the following data obtained with a Victor Meyer apparatus: weight of the liquid ethyl bromide, 0.1450 g.; volume of air expelled and collected over mercury, 33.2 ml.; atmospheric pressure, 726.6 mm.; temperature of collecting buret, 20.2°.

$$M = \frac{gRT}{pv} = \frac{0.1450 \times 0.08205 \times 293.3}{(726.6/760.0) \times 0.0332} = 110$$

The molecular weights calculated by equation (11) are usually too high (often by 1 or 2 per cent) because most gases show deviations from the simple gas law. More exact calculations can be made, as will be shown presently; but an approximate value of the molecular weight is sufficient to enable one to choose between the formula weight, obtained by chemical analysis, and some simple multiple of it.

**Deviations from the Simple Gas Law.** Only ideal or perfect gases have pressure-volume relations which are in exact agreement with the fundamental gas equation  $pv = nRT$ . In the study of physical chemistry it is frequently necessary to start with simple laws which apply strictly only to an idealized system; then deviations in actual behavior are measured; and finally the causes of the deviations are

\* Baxter and Starkweather, *Proc. Nat. Acad. Sci.*, **12**, 703 (1926).

sought. As experimental measurements were improved and as they were extended to high pressures and low temperatures, it became apparent that the simple equation was applicable to most real gases only as an approximation.

Pressure-volume data for three common gases at  $0^\circ$  are given in Table I, where the pressure  $p$  is given in atmospheres, and the volume  $V$  in liters occupied by 1 mole. If the gases were ideal and the simple gas law applicable, the product of pressure and volume should be equal at all pressures to 22.414 liters. The table shows that this product ( $pV$ ) is far from being constant and that it varies greatly for different gases. Even at 1 atm. there is a slight departure from the behavior of a perfect gas.

TABLE I  
PRESSURE-VOLUME RELATIONS OF GASES AT  $0^\circ$ <sup>1</sup>

$p$	Hydrogen		Oxygen		Carbon Dioxide	
	$V$	$pV$	$V$	$pV$	$V$	$pV$
1	22.428	22.43	22.393	22.39	22.262	22.26
50	0.4634	23.17			0.04675	2.333
100	0.2386	23.86	0.2075	20.75	0.04497	4.497
200	0.12712	25.42	0.10234	20.47	0.04285	8.571
300	0.09004	27.01	0.07184	21.55	0.04152	12.46
400	0.07163	28.65	0.05887	23.55	0.04051	16.21
600	0.05318	31.91	0.04736	28.42	0.03894	23.36
800	0.04392	35.13	0.04207	33.66	0.03779	30.23
1000	0.03837	38.37	0.03886	38.86	0.03687	36.87

<sup>1</sup> Volume in liters; pressure in atmospheres.

The influence of higher pressures is brought out clearly in Fig. 4 where  $pV$  is plotted against pressure extending out to high pressures. A low value of  $pV$  indicates that the gas is more compressible. All gases show a minimum in a  $pV$  curve unless the temperature is too high. Hydrogen and helium, which have very low boiling points, exhibit this minimum only at temperatures much below  $0^\circ$ .

The departure from ideal behavior is brought out still more clearly by plotting  $pV/RT$  against pressure as is done for nitrogen in Fig. 5. The influence of temperature as well as pressure on the departure from ideal behavior is then obvious. The values of pressure, volume, and temperature are determined experimentally. For a perfect gas this term should have a value of unity under all conditions. The behavior of nitrogen is typical of all gases. It is more compressible than a perfect gas at low pressures and less compressible at high pressures;

and the departure from ideal behavior becomes less at high temperatures and low pressures where the molecules are kept farther apart.

The deviations from the simple gas law  $pV = nRT$  can be understood better after a consideration of van der Waals' equation.

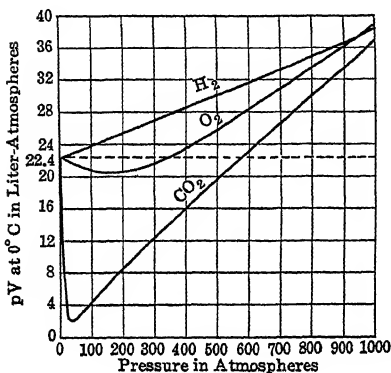


FIG 4

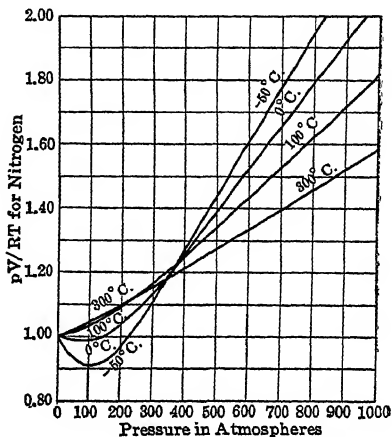


FIG. 5

**Equation of van der Waals.** In general, when a property exhibits a maximum or a minimum, at least two factors must be involved, each tending to act in opposition to the other. In the relations shown in Figs. 4 and 5 a gas is more compressible than an ideal gas because the molecules possess some attraction for each other when they are close together; on the other hand, it is less compressible because the molecules of the gas are nearly incompressible compared with the gas itself.

In 1879 van der Waals expressed these ideas quantitatively with the equation which now bears his name

$$(p + a/V^2)(V - b) = RT \quad [12]$$

The constant  $a$  represents the attractive force between the molecules and van der Waals assumed that this force varied inversely as the square of the volume. Since this force augments the pressure and thus tends to make the volume smaller, it is added to the term  $p$ . The term  $b$  represents the volume of the molecules themselves and it is subtracted from the total volume  $V$  occupied by the gas. When  $V$  is large, both  $b$  and  $a/V^2$  become negligible; and van der Waals' equation reduces to the simple gas equation  $pV = RT$ . We may predict, therefore, that any influence tending to increase  $V$  will cause the gas to approach more nearly to the ideal condition.

At low pressures the correction  $a$  for molecular attraction is more important than the correction  $b$ . At high pressures and small volumes the correction for the volume of the molecules becomes important, because this volume is relatively incompressible and constitutes an appreciable fraction of the total volume. At some intermediate pressure the two corrections counterbalance, and the gas appears to follow the relation  $pV = RT$  over a small range of pressures.

This attractive force between molecules, designated by  $a$  in van der Waals' equation, is responsible not only for the deviations from the gas laws at ordinary pressures but also for the condensation of gases to liquids, for certain types of solubility and loose compounds, and for many physical and chemical phenomena. It is electrical in character; for, although the molecules are uncharged, they contain within them positive and negative parts which can induce and attract an electrical dipole in a neighboring molecule. These charged parts of molecules attract oppositely charged units in their vicinity.

Van der Waals' constants for a few additional gases are listed in Table II.\* They can be calculated from physical chemical measurements as shown later on page 27.

TABLE II  
VAN DER WAALS' CONSTANTS  
(Units: liters, atmospheres, moles, degrees absolute)

Gas	$a$	$b$	Gas	$a$	$b$
C <sub>2</sub> H <sub>2</sub>	4.390	0.05136	CO	1.485	0.03985
NH <sub>3</sub>	4.170	0.03707	Cl <sub>2</sub>	6.493	0.05622
C <sub>2</sub> H <sub>6</sub>	18.00	0.1154	H <sub>2</sub>	0.2444	0.02661
CH <sub>4</sub>	2.253	0.04278	HCl	3.667	0.4081
CO <sub>2</sub>	3.592	0.04267	O <sub>2</sub>	1.360	0.03183
C <sub>2</sub> H <sub>4</sub>	5.489	0.06380	SO <sub>2</sub>	6.714	0.05636
C <sub>2</sub> H <sub>6</sub>	4.471	0.05714	N <sub>2</sub>	1.390	0.03913
He	0.03412	0.02370	H <sub>2</sub> O	5.464	0.03049
NO	1.340	0.02789	NO <sub>2</sub>	5.284	0.04424

*Example 3.* Calculate the pressure exerted by a mole of sulfur dioxide in 10 liters at 100° using (a) the ideal gas law and (b) van der Waals' equation.

$$(a) \ p = \frac{nRT}{V} = \frac{1 \times 0.08205 \times 373.1}{10.00} = 3.061 \text{ atm.}$$

$$(b) \ p = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{0.08205 \times 373.1}{10.00 - 0.0564} - \frac{6.714}{100.0} \\ = 3.012 \text{ atm.}$$

\* Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio.

**The Critical Temperature.** At sufficiently low temperatures a gas may be made to liquefy by applying pressure to reduce the volume and bring the molecules close enough together so that the attractive force between them will be effective. All gases have been liquefied in this way. However, there is a temperature above which it is impossible to liquefy the gas no matter how great a pressure is applied. This temperature is called the *critical temperature*; and the minimum pressure necessary to bring about liquefaction at the critical temperature is called the *critical pressure*. The volume occupied by a mole of gas or liquid at the critical temperature and pressure is called the *critical volume*.

In Fig. 6 data are shown for carbon dioxide in the neighborhood of the critical temperature. The ordinates represent pressures, and the abscissas the corresponding volumes, at constant temperature. Lines of constant temperature are called *isothermals*. For a gas which follows Boyle's law, the isothermals will be a series of right-angled hyperbolas. This condition is approximately fulfilled by air, for which three isothermals are given in the diagram. At  $48^\circ$  the isothermal for carbon dioxide is nearly of the form  $pv = k$ , but as the temperature becomes lower, the isothermals deviate more and more from those for an ideal gas. At the critical temperature,  $30.92^\circ$ , the curve is almost horizontal for a short distance, showing that for a

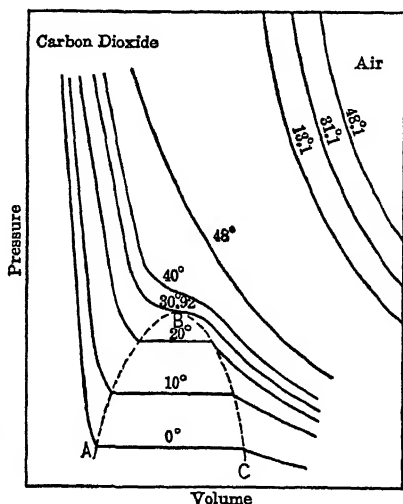


FIG. 6

very slight increase in pressure there is an enormous shrinkage in volume. At still lower temperatures, 20 and  $10^\circ$ , the horizontal portions of the curves are much more pronounced, indicating that during liquefaction there is a large decrease in volume with no change in pressure. When liquefaction is complete, the curves rise abruptly, showing that the change in volume is extremely small for a large increase in pressure; in other words, the liquefied gas is only slightly compressible. At any point within the area, indicated by the dotted line ABC, both vapor and liquid are coexistent; at any point outside, only one form of matter, either liquid or vapor, is present.

In Table III the critical temperatures  $T_c$ , pressures  $p_c$ , and volumes  $V_c$  are given for several of the common gases, arranged in order of increasing boiling points.

TABLE III  
CRITICAL CONSTANTS AND BOILING POINTS OF GASES

Gas	$T_{B.P.}$ (° K.)	$T_c$ (° K.)	$T_{B.P.}/T_c$	$p_c$ (atm.)	$V_c$ (ml./mole)	$T_{M.P.}^1$ (° K.)	$RT_c/p_c V_c$
He	4.2	5.2	0.81	2.25	61.5	0.9	3.08
H <sub>2</sub>	20.4	33.2	0.61	12.8	69.7	14.0	3.05
N <sub>2</sub>	77.3	126.0	0.61	33.5	90.0	63.2	3.42
CO	81.1	134.4	0.60	34.6	90.0	66.1	3.54
A	87.4	150.7	0.58	48.0	77.1	83.9	3.35
O <sub>2</sub>	90.1	154.3	0.58	49.7	74.4	54.7	3.42
CH <sub>4</sub>	111.7	190.2	0.59	45.6	98.8	89.1	3.47
NO	122.1	177.1	0.69	64	57.2	112.1	3.97
C <sub>2</sub> H <sub>4</sub>	169.3	282.8	0.60	50.5	126.	103.7	3.64
HCl	188.1	324.5	0.58	81.6	87.	162.1	3.75
C <sub>2</sub> H <sub>2</sub>	189.5	308.6	0.61	61.6	113	191.3	3.64
CO <sub>2</sub>	194.6	304.2	0.64	72.8	94.2	—	3.64
H <sub>2</sub> S	213.5	373.5	0.57	88.9	—	190.2	—
Cl <sub>2</sub>	238.5	417.1	0.58	76.1	123.	171.5	3.64
NH <sub>3</sub>	239.7	405.5	0.59	112.2	72.0	195.4	4.12
SO <sub>2</sub>	263.1	430.2	0.61	77.6	125.	200.4	3.64
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	342.1	507.9	0.67	29.6	367.	178.8	3.83
CCl <sub>4</sub>	349.9	556.2	0.63	45.0	276.	250.1	3.68
C <sub>2</sub> H <sub>5</sub> OH	351.6	576.2	0.68	63.0	167.	155.8	4.02
C <sub>6</sub> H <sub>6</sub>	352.7	561.6	0.63	47.9	256.	278.6	3.76
H <sub>2</sub> O	373.1	647.3	0.58	217.7	56.6	273.1	4.39
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	371.5	540	0.69	27.0	416.	183.1	3.95
CH <sub>3</sub> COOH	391.2	594.7	0.66	57.1	171.	289.7	4.99
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	397.7	570.	0.70	24.7	490.	216.6	3.86
Hg	630.0	1735.	0.36	1042.	40.1	234.2	3.40

<sup>1</sup> The melting points  $T_{M.P.}$  and ratios of boiling point to critical temperature  $T_{B.P.}/T_c$  given in these columns are not involved in the present discussions but are included for reference in a later chapter.

Several of the substances given in the table are liquids at room temperature but they become gaseous at sufficiently high temperatures. Gases which are below their critical temperatures are often called vapors. The pressure-volume-temperature relations are approximately the same for all gases, and since at the critical temperatures the liquids become indistinguishable from the corresponding gases, the  $p$ - $V$ - $T$  relations for all liquids should be the same if the liquids are compared at their critical temperatures. That this relation holds approximately is seen by examination of the last column where the value of  $RT_c/p_c V_c$  is found to be about 3.5 for many sub-

stances. With the exception of a few liquids such as water, ammonia, alcohols, and organic acids, which are abnormal as will be explained in Chapter VIII, this value ranges from 3 to 4 over a range from 4° K. to 630° K.

At any specified temperature the behavior of liquids or imperfect gases varies greatly on account of the differences in the electrical attractive forces. However, if the behavior is compared not at constant temperature and pressure, but at temperatures which are equal fractions of the critical temperature and pressure, some of the same constancy is observed which exists at the critical temperature and pressure.

A practical application of this relation is shown in Fig. 7 where  $pV/RT$  is plotted against the reduced pressure  $p/p_c$  for various temperatures, expressed as fractions of the critical temperature. This chart due to Hougen and Watson\* permits one to calculate with fair accuracy the  $p$ - $V$ - $T$  relations for any gas when the critical temperature and pressure are known. It is particularly valuable for calculations at high pressures when the constants for gas equations are not known.

*Example 4.* With the Hougen and Watson chart estimate the volume occupied by a mole of oxygen at  $-88.0^\circ\text{C.}$  and 44.7 atm. The critical temperature and pressure are found in Table III.

$$\frac{T}{T_c} = \frac{273.1 - 88.0}{154.3} = 1.20; \quad \frac{p}{p_c} = \frac{44.7}{49.7} = 0.90$$

From the chart,  $pV/RT = 0.80$ .

$$V = \frac{0.80RT}{p} = \frac{0.80 \times 0.08205 \times 185.1}{44.7} = 0.272 \text{ liters.}$$

**Van der Waals' Equation and the Critical Constants.** It will now be shown that the simple relation between the reduced critical constants follows from the equation of van der Waals

$$\left(p + \frac{a}{V^2}\right) (V - b) = RT$$

It may be expanded and rearranged in descending powers of  $V$  to give

$$V^3 - V^2\left(b + \frac{RT}{p}\right) + V\frac{a}{p} - \frac{ab}{p} = 0 \quad [13]$$

This cubic equation has three possible solutions, and for every value of  $p$  there are three different values of  $V$ ;  $a$ ,  $b$ ,  $R$ , and  $T$  being treated

\* Hougen and Watson, "Industrial Chemical Calculations," John Wiley and Sons, New York, 1936.



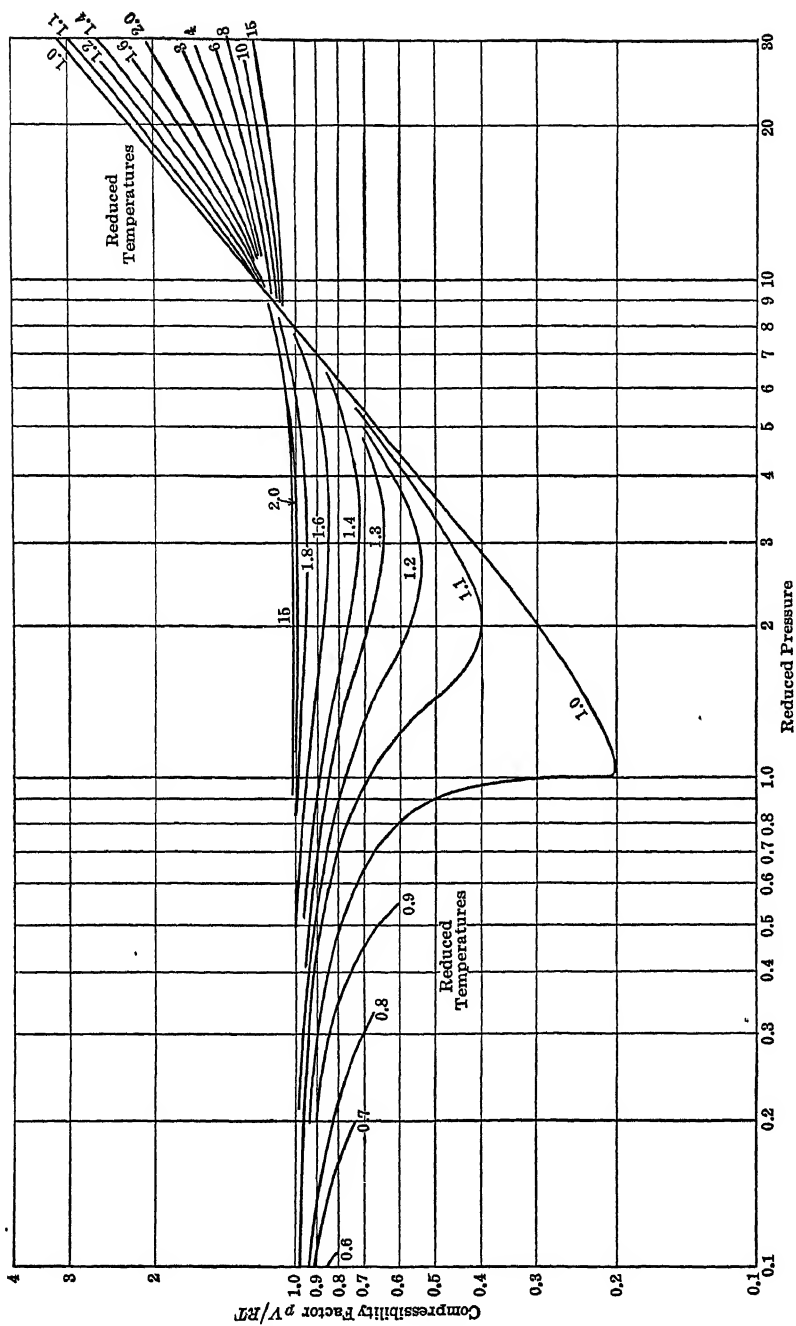


FIG. 7

as constants. The three roots of this equation are either all real, or one is real and two are imaginary, depending upon the values of the constants. That is to say, at one temperature and pressure the values of  $a$  and  $b$  may be such that  $V$  has three real values, whereas at another temperature and pressure,  $V$  may have one real and two imaginary values. In the accompanying diagram, Fig. 8, a series of graphs of the equation for different values of  $T$  is given. It will be observed that these curves bear a striking resemblance to those of carbon dioxide in Fig. 6. In the theoretical curves there are no sudden breaks such as appear in the actual discontinuous passage from the gaseous to the liquid state. Experiment has shown that the substance, instead of passing from  $B$  to  $D$  along the wavelike path  $BaCbD$ , apparently passes directly from the state  $B$  to the state  $D$  along the straight line  $BD$ . It

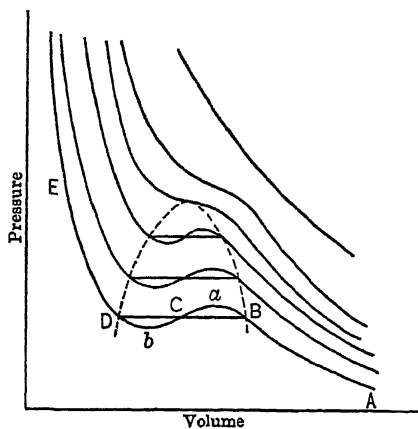


FIG. 8

is here that van der Waals' equation fails to apply. As has been pointed out, the substance between these two points is not homogeneous, being partly gaseous and partly liquid. However, by studying supersaturated vapors and superheated liquids, it has been found possible to follow the theoretical curve for short distances between  $B$  and  $D$  without discontinuity. Owing to the instability of the substance in this region, it is evident that the complete isothermal and continuous transformation of a gas into a liquid cannot be effected. The diagram shows that, as  $T$  increases, the wavelike portion of the isothermals becomes less pronounced and eventually disappears, when the points  $B$ ,  $C$ , and  $D$  coalesce. The substance at this point is in the critical condition.

It can be shown by solving equation (13) (appendix, page 660) that  $a = 3p_c V_c^2$ , that  $b = \frac{V_c}{3}$  and that  $R = \frac{8 p_c V_c}{3 T_c}$ , where  $p_c$ ,  $V_c$ , and  $T_c$  are the values at the critical point. In fact this is one of the best ways of evaluating the van der Waals constants  $a$  and  $b$ . It is not satisfactory for calculating  $R$  because this constant can be determined directly with much greater accuracy.

If, in the equation of van der Waals, the values of  $p$ ,  $V$ , and  $T$  are

expressed as fractions  $\alpha$ ,  $\beta$ , and  $\gamma$  of the corresponding critical values, then  $p = \alpha p_c$ ;  $V = \beta v_c$ ; and  $T = \gamma T_c$ . Substituting these values of  $p$ ,  $V$ , and  $T$  into van der Waals' equation (12)

$$\left( \alpha p_c + \frac{a}{(\beta v_c)^2} \right) (\beta v_c - b) = R \gamma T_c \quad [14]$$

and again substituting the values of  $a$ ,  $b$ , and  $R$  given above into equation (14)

$$\left( \alpha + \frac{3}{\beta^2} \right) (3\beta - 1) = 8\gamma \quad [15]$$

In this equation everything connected with the individual nature of the substance has vanished, thus making it applicable to all substances in the liquid or gaseous state in the same way that the fundamental gas equation is applicable to all gases, irrespective of their specific nature.

**Other Equations of State.** An equation which gives the relations between the pressure, volume, and temperature of a gas is called an equation of state. The equation of van der Waals is inconvenient to use in certain types of problems because it involves the solving of a cubic equation. The following equation, developed by Berthelot, is useful at moderate pressures

$$pv = nRT \left[ 1 + \frac{9}{128} \frac{p}{p_c} \frac{T_c}{T} \left( 1 - 6 \frac{T_c^2}{T^2} \right) \right] \quad [16]$$

In this equation  $p_c$  is the critical pressure and  $T_c$  the critical temperature (page 24). Inspection of the equation shows that, as  $T$  increases or as  $p$  decreases, it approaches the simple equation  $pv = nRT$  expressing the behavior of an ideal gas. The values of the ratio  $pv/RT$  calculated by means of this equation agree closely with those determined experimentally, provided the gases are neither associated nor dissociated and are sufficiently removed from their liquefaction temperature and pressure.

Other empirical equations of state\* are necessary to meet the demands for greater accuracy in industrial chemistry where catalytic reactions are carried out under high pressure. They involve more constants and are more cumbersome to use. The Beattie-Bridgman equation with five constants, given in the appendix on page 660, is among the more exact equations for use at high pressures.

The virial equation is finding increasing application in both theoretical and practical work with gases. According to it the deviations

\* Woolsey, *J. Chem. Educ.*, 16, 60 (1939).<sup>1</sup>

from the behavior of a perfect gas at a given temperature are a function of the pressure and a series of constants as given in the following equation

$$pV = RT + Bp + Cp^2 + \dots \quad [17]$$

These constants are evaluated from experimental  $p$ - $V$ - $T$  data but the constant  $B$  can be connected with other physical and chemical properties of the gas.

The different equations are compared in Table IV.

TABLE IV  
 $PV/RT$  FOR NITROGEN AT 1000 ATMOSPHERES

Temperature	Observed	Ideal	Van der Waals	Berthelot	Hougen and Watson Chart
0° C.	2.0632	1.0000	2.426	0.781	2.10
50° C.	1.9285	1.0000	2.182	1.071	1.95

The decision as to which equation of state should be used depends on the amount of data available and the purpose of the equation. If one desires to fit the data with great accuracy over large pressure ranges the virial equation is recommended because of its flexibility. Such an equation is really a condensed summary of the data. It requires a different set of constants for each temperature and it becomes very cumbersome for practical application. The Beattie-Bridgman equation, with five or six adjustable constants, is useful for practical purposes since it can be made to fit the data with reasonable accuracy over a considerable temperature and pressure range, but often it is not exact beyond 200 atm.

For pressures up to a few atmospheres very satisfactory results are obtainable with the equation of van der Waals or Berthelot if the critical temperature and pressure are known. The Hougen and Watson chart gives very good results even up to pressures of several hundreds of atmospheres.

**Exact Molecular Weights.** When more exact values of the molecular weights are necessary, determinations may be made at lower and lower pressures, usually by the Regnault method. The deviations from the simple gas law become less at the lower pressures and approach zero, but serious experimental difficulties are involved in weighing a large volume of gas at a low pressure. Precise measurements of densities at several low pressures can be used to determine the atomic weights of the elements which make up the molecule, with an accuracy as great as that obtainable by chemical analysis. This method is called the method of limiting densities.

As the pressure decreases, the volume increases, and the weight per liter decreases. The density  $d$  defined by  $g/v$  decreases; but the ratio of density to pressure  $d/p$  or  $g/vp$  should remain constant if the gas is perfect, since  $pv$  is constant and the total weight  $g$  remains unchanged. For ordinary gases, however, the ratio of density to

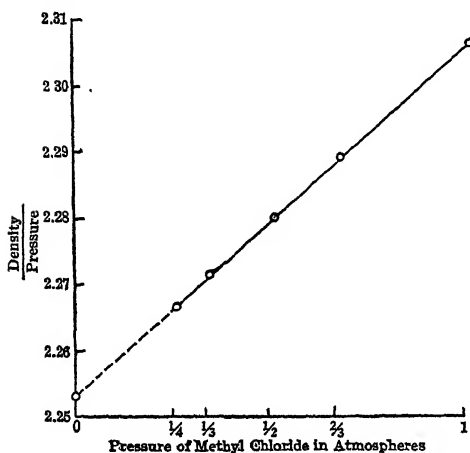


FIG. 9

pressure is not constant but decreases as the pressure decreases, as shown in Fig. 9.

For permanent gases it has been found that practically a straight line is produced when  $d/p$  is plotted against  $p$  at pressures below 1 atm. The straight line is extrapolated beyond the region of experimental measurements until it intersects the  $Y$  axis where  $p = 0$ . The intercept can be obtained mathematically from the data without graphing.

Gases which condense at fairly high temperatures show greater deviations, and the straight-line relation does not hold. More complicated mathematical formulas may then be necessary for the extrapolation.\*

Since the deviations from the perfect gas law approach zero as the pressure is reduced, the exact molecular weight  $M$  is given by the equation

$$M = \left( \frac{d}{p} \right)_0 RT \quad [18]$$

where  $(d/p)_0$  is the ratio of density to pressure extrapolated to zero pressure.

**Example 5.** Calculate the molecular weight of methyl chloride and the atomic weight of chlorine from the following data, having given the atomic weights of carbon and hydrogen:

Pressure (atmospheres)	1	$\frac{2}{3}$	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$
Density at 0° (grams per liter)	2.3074	1.5263	1.1401	0.75713	0.56660

The extrapolated ratio of density to pressure at 0° is 2.2527 as shown in Fig. 9.

\* Birge and Jenkins, *J. Chem. Phys.*, **2**, 167 (1934).

Then  $M = 2.2527 \times 0.082054 \times 273.16 = 50.492$ .

Subtracting from 50.492 the atomic weight of carbon, 12.010, and three times the atomic weight of hydrogen, 3.024, a value of 35.458 is obtained for the atomic weight of chlorine. The accepted value is 35.457.

Exact molecular weights can be obtained with the help of Berthelot's equation (page 28) or other equations of state, and they are sufficiently accurate to be used for the calculation of atomic weights over limited ranges.

*Example 6.* Calculate the atomic weight of nitrogen from the fact that the density of nitric oxide, NO, at  $0^\circ$  and 760 mm. is 1.3402 g. per liter. The critical constants are  $177.1^\circ$  K. and 64 atm.

Calculating the molecular weight  $M$  by Berthelot's equation:

$$M = \frac{g RT}{pv} \left[ 1 + \frac{9}{128} \frac{p}{p_c} \frac{T_c}{T} \left( 1 - 6 \frac{T_c^2}{T^2} \right) \right]$$

$$= \frac{(1.3402)(0.082054)(273.16)}{1 \times 1} \left[ 1 + \frac{9}{128} \frac{1}{64} \frac{177.1}{273.16} \left( 1 - 6 \frac{177.1^2}{273.16^2} \right) \right]$$

$$= 30.039 [1 - 1.12 \times 10^{-3}] = 30.005$$

The atomic weight of nitrogen =  $30.005 - 16.000 = 14.005$ . The accepted atomic weight of nitrogen is 14.008. In calculations of this type when the correction term is small, it is sufficient to calculate the correction term approximately with a slide rule.

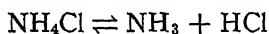
**Abnormal Densities.** The molecular weights of a great many substances have been determined by measurements of the density of the gas. Generally, they agree with the molecular weights obtained from the sum of the atomic weights. For a few substances, however, the molecular weights appeared to be quite different. Either the experimental results were in error, Avogadro's hypothesis was not universally applicable, or some new phenomenon was producing abnormal results. This situation arises frequently in the development of science. Exceptions to a general law are found, and for a time the fate of the whole law is uncertain. More exact experiments or slight corrections (such as were shown for the gas law) may save the law, or perhaps it may have to be discarded or modified. For these molecular weights, the difficulty was traced to the fact that some of the gases dissociated or broke down into smaller units or that they associated into multiples of the molecular weight.

The molecular weight of sulfur below  $500^\circ$ \* corresponds to the formula  $S_8$ ; at  $1100^\circ$  it corresponds to  $S_2$ ; and at intermediate tem-

\* As already explained, centigrade scale is meant unless otherwise specified.

peratures it may correspond to  $S_4$  or  $S_8$  or a mixture of the various forms. Iodine gives  $I_2$  from 200 to 600°; but at 1400°, and above, it has half the density and corresponds to monatomic molecules. At intermediate temperatures all densities between these two values can be obtained. Arsenic oxide, aluminum chloride, phosphorus chloride, ammonium chloride, and various other substances dissociate in a similar manner, particularly at high temperatures.

Decreasing molecular weights at higher temperatures are due to dissociation of the molecules into smaller molecules. Since the original materials are obtained on cooling, the breaking down into parts must be reversible. One of the earliest substances to be studied in this connection was ammonium chloride. It was suspected that the low molecular weight was occasioned by the reaction



the ammonia and hydrochloric acid at the high temperature occupying twice the volume of ammonium chloride vapor and giving half the density, when dissociation was complete. This interpretation was proved to be correct when it was shown that the heated vapor contained an alkaline gas and an acid gas which could be separated by fractional diffusion through a porous plug of solid ammonium chloride. The gas diffusing through the plug turned litmus paper blue. It will be shown on page 35 that gases of low molecular weight diffuse more rapidly than those of high molecular weight.

Use is made of these experimentally measured densities in calculating quantitatively the extent of the dissociation of the heavier molecules into lighter ones, as will be shown on page 277.

**Kinetic Theory of Gases.** The first attempt to explain the properties of gases on a purely mechanical basis was made by Bernoulli in 1738. Subsequently, through the labors of Kroenig, Clausius, Maxwell, Boltzmann, and others, his ideas were developed and given mathematical form as the kinetic theory of gases.

The essential feature of the kinetic theory is that heat energy in matter is a manifestation of the motion of the ultimate particles of which the matter is composed. As the temperature increases, the vibrations of a solid or liquid become more and more vigorous, until finally the heat motions cause the particles to break away from the restraining forces holding them together, and the substance vaporizes. The molecules of the gas thus formed no longer vibrate in the neighborhood of one point, but are completely separated from one another and move in straight lines with an average velocity depending on the temperature of the gas. The volume occupied by the molecules is

much smaller than the volume actually filled by them, so that a molecule can move for a considerable distance before it collides with one of its neighbors; the average distance through which a molecule moves between collisions is called its *mean free path*. The combined effect of the impacts of the moving molecules upon the walls of the containing vessel accounts for the pressure exerted by the gas. When a gas expands against an external pressure it does work at the expense of the kinetic energy of its molecules.

If the gas is insulated this loss of kinetic energy will produce a cooling effect, but if it is in thermal contact with its surroundings, heat will flow in and offset the loss of kinetic energy so that the temperature remains constant.

Starting with certain assumptions, it is possible to derive in a simple fashion an equation from which the gas laws may be deduced. Imagine  $n$  molecules, each having a mass  $m$ , confined within the cubical vessel shown in Fig. 10, the edge of which has a length  $l$  cm. Let us assume that the molecules are very small compared with the distances between them, that there are no forces between the molecules, and that the collisions of the molecules with each other and with the sides of the box are perfectly elastic. Though the different molecules are moving with different velocities and with different kinetic energies, there must be an average energy for them all. Let the velocity of the molecules having this kinetic energy be designated by  $u$ , which is the root-mean-square velocity, or the velocity obtained from the square root of  $1/n$ th of the sum of the squares of the individual velocities. As a result of their collisions with each other inside the box, the molecules will be moving sometimes in one direction, sometimes in another; since these directions may be resolved along three different axes at right angles to each other, it may be supposed that one-third of the molecules are moving always in the direction perpendicular to the wall  $A$ .

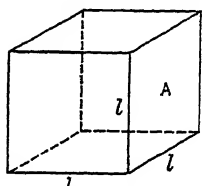


FIG. 10

Considering the collisions of molecules with  $A$ , a molecule will strike  $A$  every  $2l$  cm. as it moves back and forth across the box. If its velocity is  $u$  cm. per second, it will collide  $u/2l$  times per second with  $A$ . Since the collisions are perfectly elastic, the molecule will rebound with velocity  $-u$ , having suffered no loss in kinetic energy. Since momentum is defined as the product of mass and velocity, the momentum before collision is  $mu$  and after collision is  $-mu$ ; so that the change in momentum per collision per molecule is  $2mu$ . There are  $u/2l$  collisions per second; so the change in momentum per molecule



per second is  $mu^2/l$ . The total change in momentum per second for the  $n/3$  molecules which can collide with  $A$  is  $\frac{n}{3} \frac{mu^2}{l}$ ; this represents the average force on  $A$ , since force may be defined as the time rate of change in momentum. Pressure is force per unit area, so the pressure  $p$  on  $A$  is

$$p = \frac{\text{force}}{\text{area}} = \frac{1}{l^2} \frac{n}{3} \frac{mu^2}{l} \quad [19]$$

But  $l^3$  is the volume of the box, and we have

$$p = \frac{n}{3} \frac{mu^2}{v} \quad [20]$$

or

$$pv = \frac{1}{3} nmu^2 \quad [21]$$

This is the fundamental equation of the kinetic theory of gases. Though the equation has been derived for a cubical vessel, it is equally applicable to a vessel of any shape whatever, since the total volume may be considered to be made up of a large number of infinitesimally small cubes, for each of which the equation holds.

It must be remembered, however, that the equation applies only to gases in which there is no attraction between the molecules. It can be applied, then, only as an approximation (but a very good approximation at ordinary pressures) to real gases.

**Deductions from the Kinetic Equation.** The kinetic equation may be written in the form

$$pv = \frac{2}{3} \cdot \frac{1}{2} nmu^2 \quad [22]$$

Since the kinetic energy of a moving body is given by the expression  $\frac{1}{2}mu^2$ , the total kinetic energy of the molecules of the gas is  $\frac{1}{2}nmu^2$ . Therefore the product of the pressure and volume of the gas is equal to two-thirds the total kinetic energy of its molecules.

If the temperature of the gas remains constant, the kinetic energy of the gas remains constant, since, according to the kinetic theory, the temperature of a system is a function only of the kinetic energy of the system. The product  $p v$  must then be constant at constant temperature; this is clearly Boyle's law.

If equal volumes of two different gases are measured under the same pressure,

$$pv = \frac{1}{3} n_1 m_1 u_1^2 = \frac{1}{3} n_2 m_2 u_2^2 \quad [23]$$

where  $n_1$  and  $n_2$ ,  $m_1$  and  $m_2$ , and  $u_1$  and  $u_2$  denote the number, mass, and velocity of the molecules in the two gases. If the gases are

measured at the same temperature, the molecules of each possess the same mean kinetic energy, or

$$\frac{1}{2}m_1u_1^2 = \frac{1}{2}m_2u_2^2 \quad [24]$$

Dividing equation (23) by equation (24), we have

$$n_1 = n_2$$

or, under the same conditions of temperature and pressure, equal volumes of the two gases contain the same number of molecules. This is the hypothesis of Avogadro.

**Effusion of Gases.** If the fundamental kinetic equation is solved for  $u$  and the molar weight  $M$  is equal to  $mn$ , we have

$$u = \sqrt{\frac{3pv}{mn}} = \sqrt{\frac{3RT}{M}} \quad [25]$$

*Example 7.* What is the root-mean-square velocity of a molecule of hydrogen at  $0^\circ$ ?

$$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 273.1 \times 10^7}{2.016}} = 1.84 \times 10^5 \text{ cm. sec.}^{-1}$$

It is seen that on the average a hydrogen molecule at  $0^\circ$  travels at a rate faster than a mile per second, but it travels only an exceedingly short distance before colliding with another molecule and starting off in a different direction.

This derivation, like all those depending on the relation  $pv = RT$ , is exact only for perfect gases. Even if the expression  $\sqrt{3pv/mn}$  is used, the answer still may be erroneous (perhaps to about 1%) because in the derivation an ideal gas with no attraction between the molecules was assumed.

Relative rates of diffusion and molecular weights may be estimated from the fundamental kinetic equation. Since the density  $d$  of a gas is equal to the mass divided by the volume,  $d = mn/v$ ;

$$u = \sqrt{\frac{3pv}{mn}} = \sqrt{\frac{3p}{d}} \quad [26]$$

If the pressure and temperature of two different gases are the same the ratio of the root-mean-square velocities  $u_1$  and  $u_2$  may be calculated from the two densities,  $d_1$  and  $d_2$ , or from the molecular weights,  $M_1$  and  $M_2$ , as shown by equation (25)

$$\frac{u_1}{u_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \quad [27]$$

Under certain conditions the times required for two gases to flow through a small aperture are inversely proportional to the velocities of the molecules and hence directly proportional to the square root of the molecular weights. The proportionality is exact if the cross section of the aperture is small compared with the average distance through which a molecule travels before colliding with another molecule. At ordinary pressures this distance is so small that the conditions are no longer satisfied and a correction term is required, unless both gases happen to be of the same type — both diatomic, for example.

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 NEWITT, "The Design of High Pressure Plant and the Properties of Fluids at High Pressures," Oxford University Press, Oxford, 1940.  
 GLASTONE, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, 1940, Chapter IV.

### PROBLEMS

**NOTE.** The problems at the end of each chapter are divided into two or more sets which are separated by lines. Answers are given for only the first set. In a general way the problems of one set duplicate those of another, and it is not intended that all the problems should be worked out by any one student.

The last set, preceded by a double line, contains problems intended for students who are particularly interested.

Temperatures refer to the centigrade scale unless otherwise specified. In formulas  $T$  refers to absolute temperature;  $t$  to centigrade. When a temperature is referred to the absolute scale the fact is designated by  $K$ . Thus  $0^\circ = 273.1^\circ K$ .

If additional data are needed for solving a problem they are usually to be found in tables given in the accompanying chapter.

1. What is the volume occupied by 50.00 g. of chloroform vapor at  $100^\circ$  and 740 mm., assuming that it acts as perfect gas? *Ans.* 13.17 liter.

2. A 100-ml. flask containing an organic vapor at  $25^\circ$  is evacuated to 0.0001 mm. (of mercury). How many molecules remain in the flask? *Ans.*  $3.24 \times 10^{14}$ .

3. A certain liquid is weighed out in a Victor Meyer apparatus and vaporized. The weight of liquid is 0.110 g., the pressure 737 mm., and the temperature  $20.0^\circ$ . If the volume of displaced air, collected over mercury, is 22.5 ml., what is the molecular weight of the substance? *Ans.* 121.

4. A certain hydrocarbon is found to have a vapor density of 2.550 g. per liter at  $100^\circ$  and 760 mm. Chemical analysis shows that the substance contains one atom of carbon to one atom of hydrogen. What is its molecular formula?

*Ans.*  $C_6H_6$ .

5. Calculate the pressure exerted when 1 mole of water is heated in a volume of 10 liters to a temperature of  $150^\circ$ , using (a) the simple gas law and (b) van der Waals' equation.

*Ans.* (a) 3.47 atm.; (b) 3.43 atm.

6. The density of ammonia in grams per liter was determined at various pressures by weighing the gas in large glass bulbs. The values of  $d/p$  ( $d$  = density in grams per liter,  $p$  = pressure in atmospheres) at  $0^\circ$  were as follows: 0.77169 at 1 atm., 0.76773 at  $\frac{2}{3}$  atm., 0.76585 at  $\frac{1}{2}$  atm., 0.76383 at  $\frac{1}{3}$  atm. What is the limiting value of density/pressure at zero pressure, and what is the molecular weight of ammonia? Taking the atomic weight of hydrogen as 1.008, what is the atomic weight of nitrogen? Ans. 14.008.

7. Calculate the root-mean-square velocity of methane molecules at  $500^\circ$ .

Ans.  $1.1 \times 10^5$  cm. per sec.

8. The time of outflow of a diatomic gas through a small opening is 24.4 minutes, and the corresponding time for hydrogen is 5.5 minutes. What is the molecular weight of the gas? Ans. 39.7.

9. (a) How many grams of helium will be required to fill a circular balloon 10 ft. in diameter at  $20^\circ$  and 700 mm. pressure?

(b) What will be the volume of this gas at  $-10^\circ$  and 200 mm.?

10. A certain organic compound weighing 0.716 g. gave a volume of 242.6 ml. when vaporized at  $200^\circ$  and 750 mm. What is the molecular formula of the substance if chemical analysis shows that it must be  $C_3H_6O$  or some multiple of this formula?

11. (a) Calculate the total number of moles of air (1 mole = 28.8 g.) surrounding the earth, assuming the earth to be a sphere with a radius of 6,000,000 meters and a pressure of air everywhere on the surface amounting to 760 mm.

(b) How many tons of carbon are there in this air if the air contains 0.04 percent by volume of carbon dioxide?

12. In a Victor Meyer experiment, 0.2335 g. of a liquid was vaporized and the displaced air occupied 37.10 ml. at  $26.9^\circ$  and 740 mm. Calculate the molecular weight. The air was measured in a gas buret over water and it is necessary to subtract 26.3 mm. from the observed pressure to correct for the vapor pressure of the water.

13. (a) Calculate the van der Waals constants for acetone. The critical temperature is  $235^\circ$  and the critical pressure 35,720 mm. Calculate the pressure developed when 100 g. of acetone is placed in a liter vessel at  $100^\circ$  using (b) the simple gas laws, (c) van der Waals' equation.

14. Calculate the number of grams of hydrogen in a vessel of 500 ml. capacity when hydrogen is forced in at 100 atm. at  $200^\circ$  using (a) simple gas laws, (b) Berthelot equation, (c) Houghen and Watson chart.

15. The following values for the density of nitrogen at  $0^\circ$  have been reported by Baxter and Starkweather:

Pressure in millimeters	760	506.67	253.33
Density in grams per liter	1.25036	0.83348	0.41667

Calculate the atomic weight of nitrogen.

16. Calculate the temperature at which the root-mean-square velocity of a nitrogen molecule is the same as that of a helium molecule at  $27^\circ$ .

17. It takes an hour for the pressure of a certain evacuated vessel of 1-liter capacity to rise from 0.001 mm. to 0.002 mm. by leakage of air through a pinhole in the glass. How long will it take for chlorine at the same temperature and external pressure to leak in and raise the pressure from 0.001 mm. to 0.002 mm.?

18. A mixture of 0.1 g. of hydrogen and 0.1 g. of nitrogen is to be stored at 760 mm. pressure and  $25^{\circ}$ . What must the volume of the container be, assuming that there is no interaction between nitrogen and hydrogen?

19. One liter of a gas is contained in a balloon at  $25^{\circ}$  and 1 atm. pressure. If the gas is heated to  $35^{\circ}$ , what must be the applied pressure in order that the volume remain constant?

20. (a) Evaluate the van der Waals constants for propylene.  $p_c = 45.4$  atm.;  $v_c = 180$  ml.;  $t_c = 91.4^{\circ}$ .

(b) Calculate the pressure exerted by 1 mole of propylene at  $100^{\circ}$  when contained in a vessel having a volume of 20.06 liters, using van der Waals' equation.

(c) Calculate the same pressure assuming that  $pv = nRT$ .

21. Calculate the pressure exerted by 453.6 g. (1 lb.) of chlorine in a 10-liter vessel at  $100^{\circ}$  using (a) ideal gas law, (b) van der Waals' equation, (c) Berthelot's equation, (d) Hougen and Watson chart.

22. The ratio of the weight of 1 liter of ethyl chloride to the pressure in atmospheres at three different pressures at  $0^{\circ}$  is as follows: 2.9002 at 760 mm., 2.8919 at 475 mm., 2.8863 at 285 mm. Calculate the molecular weight of ethyl chloride and the atomic weight of chlorine by the method of limiting densities, taking the atomic weights of carbon and hydrogen as known.

23. Calculate the average kinetic energy of an oxygen molecule at  $25^{\circ}$ .

24. A 6 to 1 mixture (by volume) of neon and argon is allowed to diffuse through a small orifice into an evacuated space. What is the composition of the mixture which first passes through?

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25. The weight of a certain evacuated vessel is found to increase 0.2500, 0.5535, and 0.5268 g. when oxygen, chlorine, and a compound of oxygen and chlorine, respectively, are separately admitted into the vessel under the same conditions of temperature and pressure. Calculate from these data alone the molecular weights of chlorine and the oxide of chlorine. What can you say from these data regarding the number of atoms in the chlorine molecule?

26. How many grams of ammonia will occupy the same volume at  $-25^{\circ}$  as is occupied by 5 g. of oxygen at  $25^{\circ}$ , if the pressure is the same?

27. A glass bulb fitted with a stopcock was evacuated and found to weigh 46.8542 g. without correcting for the buoyancy of the air. When the stopcock was opened and dry air was allowed to fill the bulb, the weight increased to 47.0465 g. The barometric pressure was 745 mm. of Hg and the temperature was  $27^{\circ}$ .

(a) Calculate the total volume of the bulb from the known molecular weight of air, 28.8.

(b) Calculate the weight if the bulb were filled with dry hydrogen at this temperature and pressure.

28. A temperature scale using an ideal gas thermometer is defined by taking the melting point of mercury as zero and its normal boiling point as  $100^{\circ}$ . Calculate the normal boiling point of water and the absolute zero on this scale. Mercury boils at  $356.9^{\circ}$  and freezes at  $-38.87^{\circ}$ .

29. Calculate the pressure necessary to compress 1 mole of  $\text{CO}_2$  to a volume of 0.200 liters at a temperature of  $50^{\circ}$  using (a) the gas law:  $pv = nRT$ ; (b) The Beattie-Bridgman equation (appendix, page 660). The constants for  $\text{CO}_2$  are as follows when  $p$  is expressed in atm.,  $V$  in liters per mole, and  $T$  in  $^{\circ}\text{K}$ :  $A_0 = 5.0065$ ;  $a = 0.07132$ ;  $B_0 = 0.10476$ ;  $b = 0.07235$ ;  $c = 6.600 \times 10^6$ .

## CHAPTER III

### CRYSTALS

**Properties of Solids.** In solids there are strong forces holding the units together. Accordingly solids have a fixed shape and possess considerable mechanical strength and rigidity, and their volumes are much less dependent on temperature and pressure than are the volumes of gases. The forces may be due to direct electrical attraction between the ions, as in the sodium chloride crystal; to nonpolar bonds, as in the diamond; or to dipole attractions. In dipole attractions there may be no particular spatial arrangement or crystalline character, and such material may be thought of as a supercooled liquid in which the molecules are held together by powerful van der Waals forces.

Solids are generally classified as *crystalline* or *amorphous*. A crystalline solid is a solid in which the atoms are arranged in some definite order, constantly repeated. An amorphous solid, such as pitch or glass, may be regarded as a liquid possessing great viscosity and rigidity. In amorphous solids the physical properties (such as heat conductance, solubility, and ability to resist chemical action) are the same in all directions, whereas in crystalline solids these properties *may* have different values in different directions. When an amorphous solid is heated, it gradually softens, becomes mobile, and eventually acquires the properties characteristic of a liquid; but during this process there is no definite point of transition from the solid to the liquid state. On the other hand, when a pure crystalline solid is heated there is a sharp change from one state to the other at a definite temperature called the *melting point*.

**Crystallography.** The study of the definite geometrical forms and properties of crystalline solids is termed *crystallography*. Weiss, in 1809, showed that it is possible to consider the many different crystal forms as belonging to six systems of crystallization, with the faces referred to definite axes as shown in **Fig. 11** and described as follows:

(a) *The Regular System.* Three axes of unit length, intersecting each other at right angles.

(b) *The Tetragonal System.* Two axes of unit length and the third axis either longer or shorter, all three axes intersecting at right angles.

(c) *The Hexagonal System.* Three axes of unit length, all in the same plane and intersecting at angles of  $60^\circ$ , and a fourth axis, either longer or shorter and perpendicular to the plane of the other three.

(d) *The Rhombic System.* Three axes of unequal length, all intersecting each other at right angles.

(e) *The Monoclinic System.* Three axes of unequal length, two of which intersect at right angles, while the third axis is perpendicular to one and not to the other.

(f) *The Triclinic System.* Three axes of unequal length, no two of which intersect at right angles.

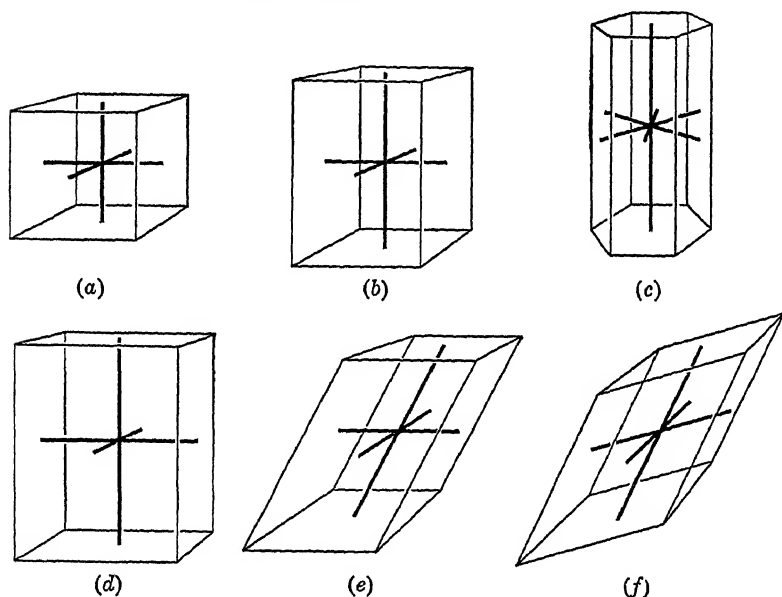


FIG. 11

The position of a plane in space is determined by three points in a system of coordinates. The position of the face of a crystal can thus be determined by its points of intersection with the three axes,  $X$ ,  $Y$ , and  $Z$ . Crystal faces are usually defined by their intercepts on the three axes in terms of the Miller indices devised in 1829. Unit distances along the  $X$ ,  $Y$ , and  $Z$  axes are termed  $a$ ,  $b$ , and  $c$ , respectively; and the Miller indices are obtained from the reciprocals of the intercepts on the axes in terms of these unit distances. In addition to the intercepts on the three crystallographic axes, the angles between the axes must be specified. In cubic crystals the axes are all at right angles and  $a = b = c$ .

Figure 12 shows the crystal axes  $X$ ,  $Y$ , and  $Z$  with a plane cutting the  $X$  axis at  $2a$ , the  $Y$  axis at  $b$ , and the  $Z$  axis at  $\frac{1}{2}c$ . The intercepts are 2, 1, and  $\frac{1}{2}$ ; their reciprocals are  $\frac{1}{2}$ , 1, and 2; and the Miller indices are written 1, 2, 4. The reciprocals of the intercepts are multiplied by an appropriate number so that no fractional numbers remain, the relative values of the intercepts being unaffected by the multiplication.

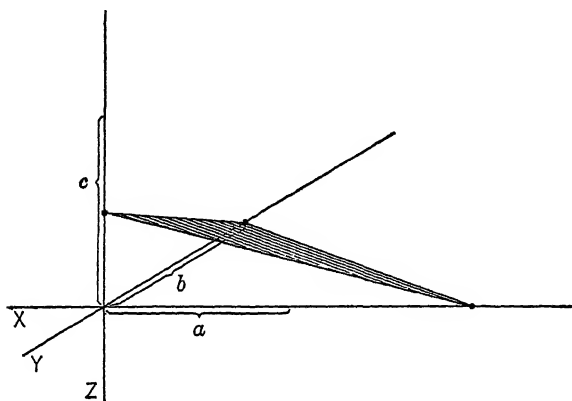


FIG. 12

The faces of crystals are usually of such a nature that the indices are small numbers: 1, 2, 3, 4, etc.; or if they are parallel to the axis, they cut it at  $\infty$  and the Miller index is zero.

According to the fundamental law of crystallography, discovered by Steno in 1669: *The angle between two given crystal faces is always the same for the same substance at a given temperature.* The fact that a crystal is characterized by constant angles affords a valuable means of identification which is used by both chemists and mineralogists.

**Properties of Crystals.** The properties of all crystals, except those belonging to the regular system, exhibit differences dependent upon the direction in which the particular measurements are made. Thus the elasticity, the thermal and electrical conductivities, and in fact all the physical properties of crystals which do not belong to the regular system have different values in different directions. Crystals in which physical properties have the same values in all directions are termed *isotropic*; those in which the values are dependent upon the direction in which the measurements are made are called *anisotropic*. Glass and certain amorphous substances, which are normally isotropic, may become anisotropic when subjected to tension or compression.

The refractive index of light may be different along different axes, except in crystals of the regular system, giving rise to the phenomenon



of double refraction. A crystal of Iceland spar ( $\text{CaCO}_3$ ) affords a beautiful illustration of double refraction. If a rhomb of this substance is placed over a piece of white paper on which there is a black spot, two spots will be seen. When the crystal is turned, one spot will remain stationary and the other spot will revolve about it. This property of Iceland spar is utilized in the construction of Nicol prisms for producing polarized light as described on page 64. When anisotropic crystals are viewed with polarized light, unique patterns of spectral colored light are produced. The appearance of these figures is so varied and characteristic as to furnish a satisfactory means of identification of many crystals. Polarizing microscopes are widely used in analytical work, especially in soil and food analysis.

The rate of solution of some crystals has been shown to be different in different directions. If the surface of a crystalline substance is highly polished and then treated for a short time with a suitable solvent, faint patterns, or *etch figures*, may appear as a result of the inequality of the rate of solution in different directions. When these figures are examined under the microscope, the crystal form generally can be determined. The examination of etch figures has come to be of prime importance to the metallographer. Thus, when an appropriate solvent is applied to the polished surface of an alloy, not only is the crystal form revealed by the etch figures but also the presence of various chemical compounds may be recognized. The etch figures developed on the surface of highly polished metal give important information as to the heat treatment and previous history of the metal. This technique has been helpful in proving with photomicrographs that a piece of metal came from a particular source. Also if the numbers stamped on a piece of metal have been filed smooth, it is frequently possible to reconstruct them by etching. The strains set up in the stamping process lead to unequal rates of reaction with the etching solution. Dilute nitric acid, picric acid, and ammoniacal copper sulfate solution are among the etching solutions used for special purposes.

A given chemical substance may sometimes exist in more than one crystal form, depending on the conditions of temperature and pressure under which the crystal is formed. Thus at temperatures above  $95.6^\circ$  sulfur crystallizes in the monoclinic system, but at lower temperatures it assumes the rhombic form. The temperature at which a crystal changes from one form into another is termed its *transition temperature*.

Two substances that crystallize in the same form with nearly identical angles are said to be *isomorphous*. Such substances are

usually similar in chemical composition. One of the best tests for isomorphism consists in placing a crystal of one substance in a supersaturated solution of another. If the crystal continues to grow the two substances are isomorphous.

**X Rays and Crystal Structure.** Important information concerning the arrangement of the atoms and molecules within crystals has been obtained from measurements of the transmission and reflection of x rays. X rays are radiations of short wavelengths of the same order of magnitude as the distance between atoms in crystals. Both can be expressed in terms of Ångström units, 1 unit being  $10^{-8}$  cm.

In 1912, Laue pointed out that the regularly arranged atoms of a crystal should act as a three-dimensional diffraction grating toward x rays. He showed mathematically that, on traversing a thin section of a crystal, a pencil of x rays should give rise to a diffraction pattern arranged symmetrically round the primary beam as a center. A photographic plate placed perpendicular to the path of the rays and behind the crystal should reveal, on development, a central spot due to the action of the primary rays and a series of symmetrically grouped spots due to the diffracted rays.

Laue's predictions were verified experimentally in the following year by Friedrich and Knipping, who obtained numerous plates showing a variety of geometrical patterns corresponding to the structural differences of the crystals examined. In Fig. 13, a Laue photograph of magnesium oxide is shown. The mathematical analysis of the Laue diffraction patterns is quite complex.

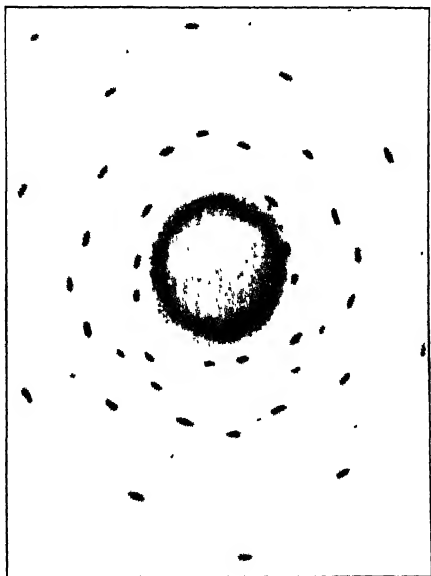


FIG. 13

The reflection or Bragg method of x-ray analysis gives results which are easier to interpret than those obtained with the Laue transmission method. W. H. Bragg and his son, W. L. Bragg, showed that the diffraction of x rays by the units of a crystal can be interpreted simply by employing the crystal as a reflection grating. The

reflection of x rays from the face of a crystal may be likened to the reflection of a beam of light from a bundle of thin glass plates of equal thickness. It is known that monochromatic light will be reflected from a bundle of plates only at definite angles, the values of which depend upon the wavelength of the incident light as well as upon the thickness of the plates. The planes of atoms or ions within the crystal correspond to the plates of glass.

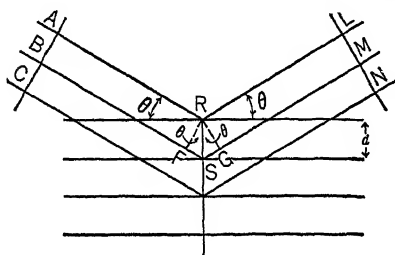


FIG. 14

A simple relation exists between the wavelength of the x rays, the distance between atomic planes in the crystal, and the angle of reflection.

Figure 14 gives the cross section of a crystal in which the horizontal lines represent a series of identical planes of atoms or ions each separated by the distance  $d$ . The plane  $ABC$  is drawn perpendicular to the incident beam of parallel, monochromatic x rays and the plane  $LMN$  is drawn perpendicular to the reflected ray. The incident beam is arranged to hit the surface of the crystal at such an angle  $\theta$  that all the light is in phase at the two planes  $ABC$  and  $LMN$ , i.e., the distance between the two along a ray is a whole-number multiple of the wave length  $\lambda$ .

It can be shown that the angle of reflection is equal to the angle of incidence. The lines  $RF$  and  $RG$  are drawn perpendicular to the beams and it can be seen that the ray  $BSM$  travels farther than the ray  $AL$  by an amount equal to  $FS + SG$ . This extra distance is equal to a whole number  $n$  of wavelengths because the angle  $\theta$  is such that the light at  $LM$  is in phase with the light at  $AB$ .

Then

$$FS + SG = n\lambda \quad [1]$$

Furthermore, since

$$\sin \theta = \frac{FS}{d} = \frac{SG}{d}$$

$$FS = SG = d \sin \theta$$

and

$$n\lambda = 2d \sin \theta \quad [2]$$

This is an important equation which gives the relation between the distance between atomic or ionic planes in a crystal and the angle at which the reflected radiation has a maximum intensity. Similar

calculations can be made for the reflection from other crystal planes lying deeper in the crystal lattice. If the rays strike the crystal at angles other than  $\theta$  the extra distance  $FS + SG$  will be such as to give fractional parts of a wavelength and there will be interference of the light reflected from the different crystal planes, which will result in a weakening of the intensity of the reflected light.

The reflection corresponding to  $n = 1$  is called the first-order reflection, the reflection corresponding to  $n = 2$  is the second-order reflection, and so on. Each successive order exhibits a wider angle and weaker intensity.

The maxima are found by rotating the crystal so as to change the angle  $\theta$  at which the x-ray beam strikes the surface. If the x rays are incident upon the face of a crystal for which  $d$  is known, the value of  $\lambda$  for the radiation used may be determined by measuring the angles at which the reflections of maximum intensity occur. On the other hand, if the wavelength of the incident radiation is known, it becomes possible to determine the spacing of the atomic planes of atoms or ions within the crystal.

The Bragg x-ray spectrometer for measuring the intensity of reflected x rays at various angles is shown in Fig. 15. In this instrument a beam of x rays passes through a filter at  $A$  and is rendered parallel by means of two narrow slits  $B$  and  $B'$ . After passing through these slits, the rays are reflected from one of the faces of a crystal  $C$ , which is mounted as a reflection grating upon the table of the spectrometer; and the reflected beam then passes through a slit  $D$  and enters an ionization chamber where its intensity is measured.

The ionization chamber contains two electrodes connected to a high-voltage battery through an electrometer. The space between the electrodes is filled with sulfur dioxide or other gas which is easily ionized by x rays. The magnitude of the electrometer deflection depends on the number of ions formed, which, in turn, is a measure of the intensity of the x rays. The crystal and the ionization chamber are rotated about a common axis, the angle between the face of the crystal and the slit of the ionization chamber being maintained the

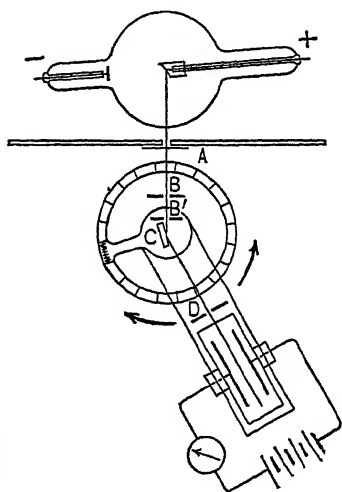


FIG. 15

same as that between the face of the crystal and the incident beam. The intensity of the ionization corresponding to successive settings of the crystal is measured, and from these readings the angles corresponding to the maximum deflections are determined.

**The Structure of Cubic Crystals.** The regular or cubic system is the simplest, but there are three possible arrangements or *space lattices* of the fundamental structural units. These are known as the *simple cubic*, the *face-centered cubic*, and the *body-centered cubic* lattices.

The structures characteristic of the three cubic lattices are shown diagrammatically in Figs. 16, 17, and 18. It will be observed that,

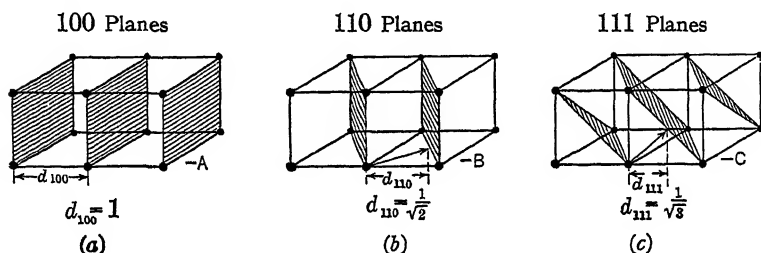


FIG. 16. Simple Cubic Lattice.

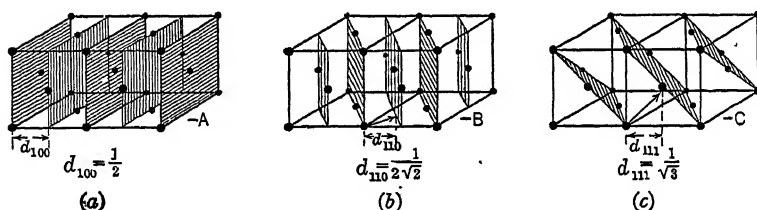


FIG. 17. Face-Centered Cubic Lattice.

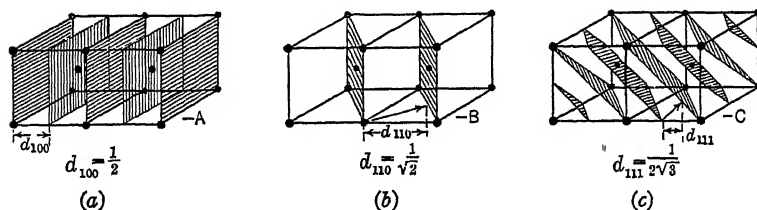


FIG. 18. Body-Centered Cubic Lattice.

in the simple cubic lattice, a single structural unit, represented by a black dot, is situated at each corner of the cubic cell. In the face-centered lattice, there is one unit situated at each corner of the cubic cell and also one unit in the center of each face. In the body-centered

lattice, there is one unit at each corner and also one unit at the center of the cubic cell. Through the use of x rays it is possible to determine the distances between the different sets of planes in a given cubic crystal and to determine to which of the three types the crystal belongs.

In the simple cubic lattice shown in Fig. 16*a*, the (100) planes cut the  $X$  axis and are parallel to the  $Y$  and  $Z$  axes. In Fig. 16*b*, the (110) planes run obliquely across the  $X$  and  $Y$  axes but cut the  $Z$  axis at infinity, i.e., they are parallel to the  $Z$  axis. The Miller indices for such a plane are 110, as already explained. In Fig. 16*c*, the planes cut obliquely across all three axes, intercepting each at the same distance from the origin and giving the Miller indices 111. The distance between (100) planes,  $d_{100}$ , is obviously the length of a face or 1. The perpendicular distance between the (110) planes,  $d_{110}$ , is half the diagonal of a face,  $\sqrt{2}/2$  or  $1/\sqrt{2}$ . The perpendicular distance between the 111 planes,  $d_{111}$ , is  $1/\sqrt{3}$ , a fact which is demonstrated geometrically on page 661 of the appendix.

In the face-centered cubic lattice additional (100) planes can be passed through the black dots representing the crystal units as shown in Fig. 17*a* by vertical shading. They pass vertically through the center of the front and back faces, and the distance between planes,  $d_{100}$ , is now  $1/2$  on the assumption that  $d_{100}$  for the simple lattice is 1. A new set of (110) planes also can be passed through the face-centered cubic lattice as shown in Fig. 17*b*. These additional planes with vertical shading include the units in the centers of the front and side faces and come midway between the planes of the simple cubic lattice. The distance between planes then is one-half as great as it is in the simple cubic lattice, and  $d_{110}$  is  $1/2 \times 1/\sqrt{2}$ . The (111) planes of the simple lattice already pass through the centers of all the faces of the face-centered lattice as shown in Fig. 17*c*, and no new planes can be introduced. The distance between planes,  $d_{111}$ , is then the same as in the simple lattice, namely,  $1/\sqrt{3}$ .

In the body-centered cubic lattice additional (100) planes can be passed through the units in the centers of the cube as indicated with vertical shading in Fig. 18*a*. These new planes are halfway between the planes of the simple lattice, and  $d_{100} = 1/2$ . The (110) planes, as shown in Fig. 18*b*, already pass through the unit in the center of the cube, so that no new planes are possible. The value of  $d_{110}$  is then the same as it was in the simple cubic lattice, namely,  $1/\sqrt{2}$ . The (111) planes, as shown in Fig. 18*c*, do not pass through the central units; and it is possible to insert another set of planes through these units midway between the (111) planes of the simple lattice, as indi-

cated with opposite shading. The distance between planes then is half as great and  $d_{111} = 1/2 \times 1/\sqrt{3}$ .

The ratios of the distances between the three different sets of planes in the three different types of cubes can now be summarized.

Simple cubic,

$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.578 \quad [3]$$

Face-centered cubic,

$$d_{100} : d_{110} : d_{111} = \frac{1}{2} : \frac{1}{2\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1 : 0.707 : 1.155 \quad [4]$$

Body-centered cubic,

$$d_{100} : d_{110} : d_{111} = \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} = 1 : \frac{2}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 1.414 : 0.578 \quad [5]$$

In the following section it will be shown how x rays can be used to determine which of these possible structures a crystal actually has.

**Crystal Structure of Sodium Chloride.** From the external symmetry of sodium chloride crystals it is known that this substance belongs to the cubic or regular system. The lattice type then must be either simple cubic, face-centered cubic or body-centered cubic; but to decide which of these three is correct an x-ray study is necessary.

The positions of the maximum reflections from the (100), (110), and (111) faces of a crystal of sodium chloride, obtained with an x-ray tube having a palladium target, are shown in Fig. 19. The

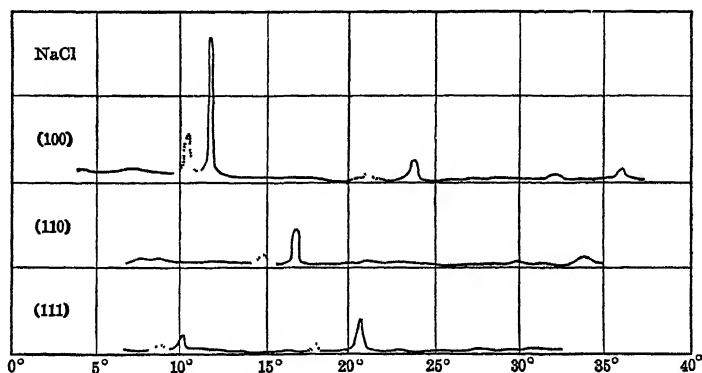


FIG. 19

ordinates represent intensities of ionization as measured by the electrometer. The abscissas represent the degrees through which the

ionization table is turned starting from a point in line with the slits. These angles must be divided by 2 to obtain the angle,  $\theta$ , of reflection from the crystal, because the crystal face itself is inclined toward the incident light and the angle of reflection is equal to the angle of incidence. The first-order reflections for the planes are found to occur at spectrometer readings\* of  $11.8^\circ$ ,  $16.8^\circ$ , and  $10.4^\circ$  for the (100), (110), and (111) planes, respectively, corresponding to values of  $\theta$  of 5.9, 8.4, and 5.2.

Taking the ratio of the sines of these angles,

$$\sin 5.9^\circ : \sin 8.4^\circ : \sin 5.2^\circ = 0.103 : 0.146 : 0.091 = 1 : 1.42 : 0.88$$

and since

$$d = \frac{n\lambda}{2 \sin \theta}$$

it follows that the corresponding values of  $d$  should be in the ratio of the reciprocals of these numbers; i.e.,

$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{1.42} : \frac{1}{0.88} = 1 : 0.704 : 1.14$$

But we have already seen that for a face-centered cubic crystal

$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1 : 0.707 : 1.155$$

Therefore, the fundamental space lattice of a crystal of sodium chloride must be face-centered.

In this calculation only the first-order reflections were used, where  $n = 1$ . Higher order reflection maxima corresponding to values of  $n$  of 2 and 3, etc., are obtained also, but the higher orders usually become less intense. In the (100) plane in rock salt, shown in Fig. 19, there is a first-order spectrum at 11.8, a second-order at 23.7, and a third-order at approximately 36.3. Taking half of these angles,  $\theta = 5.9^\circ$ ,  $11.85^\circ$ , and  $18.15^\circ$ ; and

$$\sin \theta_1 : \sin \theta_2 : \sin \theta_3 = 0.103 : 0.205 : 0.312$$

These numbers are very close to the theoretical ratios, 1 : 2 : 3.

From these data the interplanar distance,  $d_{100}$  is calculated in terms of the wavelength. Thus the value of  $n\lambda/(2 \sin \theta)$  is  $4.85\lambda$ , as obtained by averaging  $1\lambda/(2 \times 0.103)$ ,  $2\lambda/(2 \times 0.205)$ , and  $3\lambda/(2 \times 0.312)$ . The distance in Ångströms can be readily calculated when the wavelength,  $\lambda$ , of the x rays is determined.

\* The dotted maxima are due to a second x-ray exciting line.



Second-order reflection maxima are apparent also in the graph for the (110) plane at  $33.6^\circ$  ( $\theta = 16.8$ ) and for the (111) plane at  $20.8^\circ$  ( $\theta = 10.4$ ).

The crystal lattice might be made up of sodium chloride molecules as units, or the parts of the molecule might be separated to give a lattice of sodium atoms or ions, interpenetrating a lattice of chloride atoms or ions. A great deal of evidence, particularly relative intensities of x-ray reflections from various planes, supports the view that two separate lattices are involved in sodium chloride and that the sodium ions alternate with chloride ions in the crystal. In this type of crystal the identity of the molecules becomes lost, each sodium atom belonging equally well to six chlorine ions and each chlorine atom to six sodium ions. If the term molecule is applied at all, it might be used with

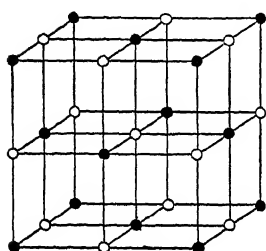


Fig. 20

reference to the whole crystal. Some types of crystals, however, do have groups of atoms, like molecules, for the units of their crystal lattice.

The sodium chloride lattice is indicated in Fig. 20, where the black circles represent chloride ions and the white circles represent sodium ions. They are not drawn to scale. In reality the ions are relatively larger so that they practically touch each other.

This interpenetrating lattice is strongly supported by the facts shown in Fig. 19. Indeed, they have not been explained in any other way.

It will be noted in Fig. 19 that for the (111) plane the first-order maximum is very weak, the second-order is intense, and the third-order is missing. Also from Fig. 20 it will be seen that the (100) and (110) planes contain an equal number of sodium and chloride ions, but that in the (111) planes, alternate planes contain only sodium ions and only chloride ions. When x rays are reflected from the (111) planes at such angles that the rays from successive planes of chloride ions differ in path length by one wavelength, the rays coming from the planes of sodium ions midway between will be out of phase with those from the chloride planes by half a wavelength, causing interference. The interference would be complete except for the fact that the chloride ions are 50 per cent heavier\* than the sodium ions, and so the x-ray reflections from them are more intense. The reflections for the first-order spectrum are still present but they are much weakened. For the second-order spectrum there is a difference of a whole

\* The reflection is determined by the number and distribution of electrons, but these, in turn, are roughly proportional to the atomic weight.

wavelength between the rays from the chloride and sodium planes, and consequently there is no interference. The curve in Fig. 19 for the (111) plane shows that the second-order maximum has its full intensity. The third-order spectrum again corresponds to a difference of a wavelength and a half, and the interference causes the practical disappearance of the maximum. This interpretation of the curves through the interpenetrating lattices is further substantiated by the fact that in potassium chloride, which also crystallizes in the same type of lattice, the ions of chlorine and potassium have approximately the same atomic weight and number of electrons. The first- and third-order maxima are entirely missing in the (111) planes. Potassium bromide, however, with unlike atomic weights gives again a definite but weakened maximum for the first order.

**Crystal Structural Units.** The crystal structure of sodium chloride has been worked out in detail to illustrate the use of x-rays in determining the type of lattice. In general the analysis of the structure of a crystal involves assignment to a particular type of symmetry, calculation of the distances in the lattice structure, and determination of the number of atoms in a unit cell. There are 230 different standard groups to which the crystal may belong, and the decision of the correct structure is based on the angles of x-ray reflections and the relative intensities.

The particular crystal structure which will be taken by a given element or compound depends partly on the size of the ion and on the charge of the nucleus, i.e., the atomic number as described on page 626. The ions may be composed of single atoms or of groups of atoms. There are different standard types of structure for elements where all atoms are the same, and for compounds such as  $AB$ ,  $AB_2$ ,  $AB_3$ , and others.

The three types of cubic crystals, simple, face-centered, and body-centered, were shown in Figs. 16, 17, and 18. An example of interpenetrating, face-centered cubic lattices was shown in Fig. 20. A few other typical lattices are shown in Fig. 21.

The *cesium chloride* ( $CsCl$ ) type of lattice consists of two interpenetrating simple cubic lattices. Each cube of eight chloride ions has at its center a cesium ion, and likewise each cube of eight cesium ions has at its center one chloride ion. The result is a body-centered lattice with each ion equidistant from eight other ions of the opposite charge.

The *zinc sulfide* ( $ZnS$ ) lattice (or the diamond lattice) is somewhat like the sodium chloride lattice in that it consists of two interpenetrating face-centered cubic lattices. The crystal structure of the diamond

is of the same lattice type except, of course, that all the atoms of the whole lattice are of the same kind. Each carbon atom is surrounded by four other carbon atoms in the tetrahedral arrangement for carbon familiar in organic chemistry. Four tetrahedrons of the crystal lattice meet at every carbon atom, except at the surface, making a continuous lattice, so that the crystal may be regarded as one large molecule.

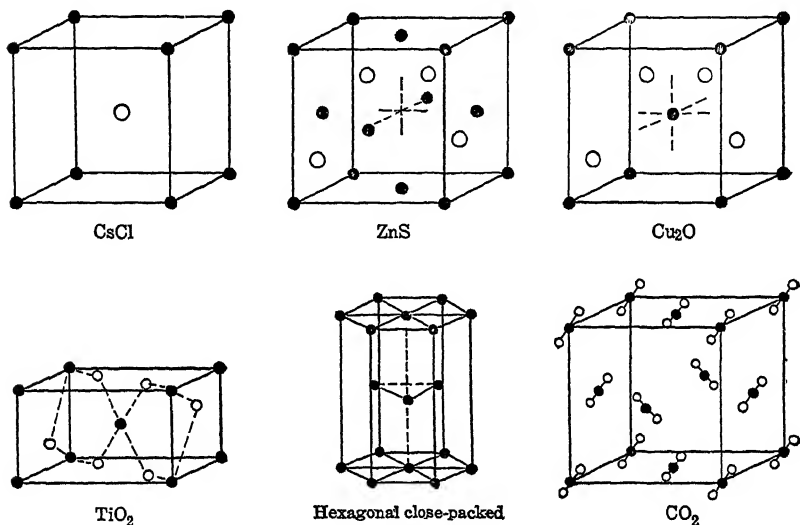


FIG. 21

In the *cuprous oxide* ( $\text{Cu}_2\text{O}$ ) arrangement, the oxygen atoms are arranged on a body-centered cubic lattice, and the cube can then be divided into eight smaller cubes, each touching the central atom at one corner. The copper atoms are arranged on a lattice which penetrates the oxygen lattice so that the copper atoms come at the centers of the alternate, small cubes.

The *rutile* ( $\text{TiO}_2$ ) lattice illustrates the tetragonal lattice in which only two of the axes are of the same length.

The *close-packed hexagonal* lattice is another example of a lattice which is not cubical. It is obtained by placing together six prisms having equilateral triangles as bases. Seven atoms are placed at the top and bottom hexagons thus formed, and three additional atoms are placed in the centers of alternate prisms. Hexagonal close-packing is one of the stable ways in which hard spheres can be forced close together. The structure is similar to that in which three spheres touch to form a triangle; a single sphere is piled on top, then another

group of three, and so on. Thus, alternating layers of three and one are built up. This structure is found in several metals.

The units of a crystal lattice are not necessarily atoms or monatomic ions. They may be molecules as, for example, in *carbon dioxide* ( $\text{CO}_2$ ), where a carbon atom is joined firmly to two oxygen atoms and placed at the eight corners and at the centers of six faces of a cube. The forces holding these molecular crystals together are very weak. The carbon dioxide crystal, for example, is stable only at low temperatures, and when it vaporizes, the atoms in a given molecule stay together as a unit. Many of the low-melting organic compounds are of this molecular type. In the ionic lattices such as sodium chloride there is no union to form molecules in the crystal.

Still another type of lattice, not shown in Fig. 21, is represented by calcium carbonate, sodium nitrate, and other salts. Three oxygen atoms are closely held by carbon atoms, giving carbonate ions which occupy definite positions as units in the crystal lattice. The calcium ions fill up the remainder of the lattice. A carbonate ion does not "belong" to a given calcium ion, but three particular oxygen atoms belong definitely to a given carbon atom.

Considerable progress has been made in correlating lattice types with atomic or ionic radii. For example, in crystals of  $AB_2$ , the rutile type of lattice is formed when the ionic radius of  $A$  is 43 per cent of that of  $B$ ; but when it is 67 per cent, the crystal lattice is of a different type.

**Structure and Properties of Crystals.** Many of the properties of crystals can be interpreted in terms of the crystal structure. Only a few examples can be cited. The face-centered and the hexagonal close-packed crystals give arrangements of greatest density with the atoms closest together. If a pile of hard spheres of the same diameter is compressed into the smallest possible space, the packing will follow one of these two arrangements or a similar one in which the density is just as great. Most elements tend to crystallize in these forms.

In isomorphous crystals one ion can replace another, but such a displacement is possible only when the crystal lattices are of the same type and the ionic radii are of approximately the same magnitude.

The great difference between graphite and diamond can be understood in terms of the crystal lattice. In the diamond every carbon atom is equidistant from four other carbon atoms and the crystal is hard and perfect. Graphite has hexagonal networks in sheets resembling benzene rings of organic chemistry. The distances between atoms in the plane is  $1.4 \text{ \AA}$ ., but the distance between these sheets is  $3.41 \text{ \AA}$ . In two directions, then, the carbon atoms are tightly held

as in the diamond, but in the third direction the force of attraction is much less. This gives a structure such that one layer can slip over another. The crystals are less perfect and flaky, and yet the material is not wholly disintegrated under mechanical rubbing. It is excellent then as a lubricant. Other lubricants also are found to have a layer crystal structure.

Crystals may be classified not only according to the type of geometrical lattice but also according to the type of binding. Table I is suggestive.

TABLE I  
CLASSIFICATION OF CRYSTALS BY TYPE OF BINDING<sup>1</sup>

Type	Binding	Example	Properties
Ionic	Electrostatic	NaCl, CaF <sub>2</sub> , CaCO <sub>3</sub>	Fairly high melting point
Silicate	Weak electrostatic	Al <sub>2</sub> SiO <sub>5</sub> , Mg <sub>2</sub> SiO <sub>2</sub>	High melting point; glassy
Homopolar	Electron-pair bond	ZnS, diamond	Hard. Very high melting point
Molecular	Dipole attraction and van der Waals forces	CO <sub>2</sub> , argon, CCl <sub>4</sub> , ice	Low melting point
Layer	Ionic or homopolar; dipole attraction between layers	Graphite, CdI <sub>2</sub>	Cleavage planes
Metallic	Positive ions and free electrons	Cu, Zn, Fe	Electrically conducting
Metalloidal	Metal ions with sulfur, arsenic, etc.	FeS, FeS <sub>2</sub> , NiAs	Decomposition at high temperatures

<sup>1</sup> Stillwell, *J. Chem. Education*, **10**, 599 (1933).

**Calculation of the Wavelength of X Rays.** The structure of a crystal can be determined from relative measurements with x rays as already described. It is possible, also, to obtain the absolute value of the wavelength  $\lambda$  using a simple crystal such as sodium chloride. In the elementary cubic cell of NaCl there is one chloride ion at each corner and also one chloride ion at the center of each face. Since each one of the corner ions is common to eight similar adjacent cubic cells, only one-eighth of its mass can be considered as belonging to any one of the eight cells. In like manner, each face-centered ion is common to two adjacent cubes and hence contributes only one-half of its mass to each of the two cubes. Therefore, the eight corner ions contribute the mass of one ion, and the six center ions contribute the mass of three

ions to a single cubic cell. In other words, the total mass of chlorine associated with a single cubic cell is equal to the mass of only four chloride ions. In precisely the same way, it may be shown that the mass of four sodium ions is also associated with a single cubic cell, and each cell may be considered as having a mass equal to that of four molecules of sodium chloride. Since the volume of a gram-molecule of sodium chloride is 27.0 ml., it follows that the volume associated with four molecules, or the volume of a single cubic cell, is

$$4 \times 27.0 / 6.02 \times 10^{23} = 179 \times 10^{-24} \text{ ml.} \quad [6]$$

where  $6.02 \times 10^{23}$  is Avogadro's constant, i.e., the actual number of molecules in one gram-molecule of sodium chloride. The length of the edge of the cell is found to be  $5.64 \times 10^{-8}$  cm. by extracting the cube root of  $179 \times 10^{-24}$ . The distance between the planes parallel to the (100) face,  $d_{100}$ , will be one-half of this number, or  $2.82 \times 10^{-8}$  cm.

Having determined the value of  $d_{100}$  and having previously found that  $d_{100} = 4.85\lambda$  for x rays from a palladium target, it is easily calculated that

$$\lambda = 2.82 \times 10^{-8} / 4.85 = 0.58 \times 10^{-8} \text{ cm.} \quad [7]$$

It is possible, therefore, to determine the wavelength of x rays by means of a crystal of known structure in precisely the same manner as in the determination of wavelengths of light by means of a diffraction grating.

The wavelength of the x rays having thus been found, the interplanar distance in other crystals may be determined by simple application of the formula  $n\lambda = 2d \sin \theta$  in the manner already illustrated.

The wavelengths of x rays can also be determined by diffraction of x rays from ruled gratings. The equation applied in this case is

$$n\lambda = d(\cos \theta + \cos \phi)$$

where  $\theta$  and  $\phi$  are the very small angles (less than one degree) which the incident and diffracted beams, respectively, make with the face of the grating;  $d$  is the distance between the lines mechanically ruled on the face of the grating. With wavelengths obtained in this way the calculation given in the preceding paragraphs can be reversed to give Avogadro's number. In fact, the value of Avogadro's number now considered most accurate is obtained by application of this procedure to calcite crystals ( $\text{CaCO}_3$ ).

**The Powder Method of X-Ray Analysis.** In the Bragg method just described, a movable ionization chamber was used to determine the

position and intensity of the reflection maxima. Sometimes a strip of photographic film is substituted for the ionization chamber. It is then necessary to rotate the crystal by some type of clockwork mechanism so that the planes of the crystal lattice are sure to be set at the proper angle during part of the time in order to record the maxima in the reflection. Instead of rotating one large crystal, the same results may be achieved by using many small crystals orientated in all directions. This method was devised almost simultaneously by A. W. Hull and by Debye and Scherrer.

A small beam of parallel monochromatic x rays is allowed to pass through a finely divided crystalline substance, and a characteristic spectrum, made up of fine lines, is produced upon a properly placed photographic film. These lines correspond to the reflections from the different faces of the minute crystalline particles of the powdered substance. The method of powders is much simpler and more rapid than the reflection method. Furthermore, instead of a well-developed crystal of appreciable size, a very small amount of crystalline powder is all that is required; in fact, Hull has found that the amount of material necessary for a complete determination of crystal structure need not be more than 1 cu. mm. A typical spectrogram is reproduced in Fig. 22.

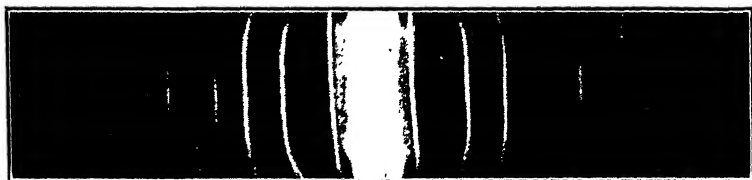


FIG. 22

If the powder under examination consists of a large number of minute cubical crystals orientated in all possible directions, some of the crystals will be so placed as to reflect rays from their (100) planes, others from their (110) planes, and still others from their (111) planes. But in each case the reflection will take place at a definite angle and will give rise to a series of lines on the film corresponding to the reflection maxima for each set of planes. Only those crystals whose faces lie at the proper angle cause reflection of the x rays; the remaining crystals give rise to interference of the light reflected from the different layers. Of course, there will be several sets of lines each depending upon the order of reflection.

The spacing and intensity of these lines are characteristic of a given

crystalline substance. In mineralogy these powder spectrograms are valuable for identification, and in metallography they give important information regarding the structure of metals and alloys.

The powder method has been applied to the analysis of mixtures of salts. For example, chemical analysis may reveal the presence of sodium, potassium, chlorine, and bromine in a given sample, and it is necessary to know whether sodium chloride and potassium bromide, or potassium chloride and sodium bromide, or all four salts are present in the mixture. Although this question cannot be answered by ordinary chemical analysis, Hull has shown that x-ray analysis offers an easy solution of the problem. An x-ray photograph of the mixed crystalline powder furnishes a set of lines from which it is possible to determine the composition of the mixture by comparison with similar photographs made with the pure salts alone. Furthermore, by studying the relative intensities of the lines, it is even possible to estimate roughly the amounts of each salt present in the mixture.

**Miscellaneous Applications of X Rays.** The x-ray analysis of crystals finds many practical applications in different fields.

Similarities in crystal form among different compounds, such as that between sodium nitrate and calcium carbonate, are readily revealed by x-ray analysis. This test is more reliable than the older tests for isomorphism.

In organic chemistry the long chains and benzene rings which have been used in structural formulas now find experimental support from the data of x rays. As more  $\text{CH}_2$  groups are added to a chain, the length of the crystal unit increases approximately  $1.3 \text{ \AA}$ . for each carbon atom, but the cross section remains nearly constant. The hydrocarbon  $\text{C}_{17}\text{H}_{36}$ , for example, has a length of  $24.3 \text{ \AA}$ . in the crystal lattice, whereas the hydrocarbon  $\text{C}_{35}\text{H}_{72}$  has a length of  $47.7 \text{ \AA}$ .

Crystals which have only a slight degree of symmetry are difficult to interpret and to study with x rays because the crystals are poorly formed and the planes ill defined. In the examination of organic compounds and crystals containing light elements it is desirable to use soft x rays produced with a target of copper or other light metal, because the x rays produced by targets of heavy metals are too penetrating.

X ray absorption varies with the density of the absorbing solid, and a dense object leaves a shadow on a photographic plate placed behind it. This property is utilized in the setting of bones, the extraction of teeth, the search for abnormal growths, and the location of internal cracks or blowholes in castings. The detection of smuggled diamonds or of stray metal objects in food products and the examina-



tion of oranges for frost injury before packing are among the many uses to which x rays are put.

Many metallurgical operations can now be studied more scientifically through the use of x rays. Metals have simple crystal lattices and are ductile, whereas the lattices of non-metals are more complex and the material is less ductile. Different crystal forms produced by different heat treatments are readily recognized. Iron carbide, for example, when cooled slowly, shows lines which are not present when it is cooled rapidly.

Even material which is not ordinarily classed as crystalline may be tested with x rays, for example, fibers, rubber, shellac, cellulose compounds, and asbestos. A photograph through a pinhole with monochromatic x rays gives concentric rings for powders and symmetrical arcs for fibers.

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### PROBLEMS

1. A certain crystal face intercepts the  $X$  axis at  $\frac{1}{2}a$ , the  $Y$  axis at  $b$ , and the  $Z$  axis at  $\frac{2}{3}c$ . What are the Miller indices of this face? *Ans.* 4, 2, 3.
2. In the reflection of x rays of wavelength  $0.643 \text{ \AA}$ . by a certain crystal, first-order maxima for the (100), (110), and (111) planes are obtained when  $\theta$  is  $7^\circ 41'$ ,  $5^\circ 26'$ ,  $13^\circ 34'$ , respectively. (a) What are the values of  $d_{100}$ ,  $d_{110}$ , and  $d_{111}$ , and (b) what type of lattice has this crystal?  
*Ans.* (a)  $d_{100} = 2.40 \times 10^{-8} \text{ cm.}$ ; (b) body-centered cubic.
3. Potassium bromide has a lattice which is equivalent to a face-centered cubic lattice and the edge of the unit cube is  $6.54 \text{ \AA}$ . The unit contains the equivalent of 4 ions of each kind. What is the density of the crystal? *Ans.* 2.83.
4. Cesium bromide crystallizes as if it were a body-centered cubic. In the Bragg spectrometer using x rays of  $0.576 \text{ \AA}$ . a first-order maximum for the (100) plane is

obtained at an angle of  $\theta$  of  $7^\circ 43'$ . What is the interplanar distance  $d_{100}$ ? The length of the unit cell is  $2 \times d_{100}$ , and it contains the equivalent of one molecule of CsBr. What is the density of the cesium bromide? *Ans.* 4.49.

---

5. The Miller indices of three faces of a cubic crystal are (100), (010), and (001).

(a) What are the intercepts of the three faces?

(b) Sketch the crystal showing these three faces.

6. Calcium oxide was examined with x rays having a wavelength of  $0.576 \text{ \AA}$ . First-order maxima were observed for the (100) plane at  $\theta = 6^\circ 54'$ , for the (110) plane at  $9^\circ 52'$ , and for the (111) plane at  $6^\circ 00'$ . What are the values of  $d_{100}$ ,  $d_{110}$ , and  $d_{111}$  and what type of lattice does this crystal have?

7. A substance crystallizes in a form analogous to that of sodium chloride. Its density is 1.984 g. per ml. and its molecular weight is 74.56. What is the length of the edge of a single cell?

8. The crystal unit cell of MgO is a cube  $4.20 \text{ \AA}$ . on an edge. Each cell contains the equivalent of 4 atoms of magnesium and 4 of oxygen. What is the density of crystalline magnesium oxide?

---

9. Metallic iron investigated with monochromatic x rays from an unknown source showed, at  $20^\circ$ , first-order reflection maxima at  $\theta = 11^\circ 36'$ ,  $8^\circ 3'$ , and  $20^\circ 26'$  in the (100), (110), and (111) planes respectively. At  $1100^\circ$  the maxima occurred at  $9^\circ 8'$ ,  $12^\circ 57'$ , and  $7^\circ 55'$ .

(a) What do these results show concerning the allotropic modifications of iron stable at these two temperatures?

(b) Calculate  $d_{100}$  for the  $20^\circ$  form. The density of iron at  $20^\circ$  is 7.86.

(c) Calculate the wavelength of the x rays used.

(d) What is the density of iron at  $1100^\circ$ ?

## CHAPTER IV

### PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

A physical property, such as molecular weight, which depends on the number and kind of atoms in the molecule is called an *additive* property. A physical property, such as the optical rotation of light, which depends on the particular arrangement of atoms within the molecule is called a *constitutive* property. A great many physical-chemical properties are additive in part and constitutive in part. The prediction of physical properties from the known constitution is valuable from both a practical and a theoretical viewpoint. Likewise these physical properties are useful in identifying chemical substances and deciding questions of their molecular structure.

The rigid bonds which hold organic molecules together make definite constitutions possible, whereas the mobility of ions in solution prevents a definite spatial structure. This chapter, therefore, is concerned chiefly with the materials of organic chemistry.

**Refractive Index.** The extent to which a beam of light is bent or refracted when it passes from one substance into another depends on the change in concentration of atoms in the path of the light, on the kind of atoms, and on the arrangement of atoms within the molecules. Accordingly, the refractive index, which is a quantitative measure of this refraction of light, may be used to determine concentration of materials, to establish the identity and purity of a chemical compound, or to ascertain the arrangement of atoms within the molecule.

The index of refraction  $n$  is defined by the equation

$$n = \frac{\sin i}{\sin r} \quad [1]$$

where  $i$  is the angle of incidence and  $r$  is the angle of refraction, each measured by reference to a line perpendicular to the surface. The index of refraction is also equal to the ratio of the velocity of light in a vacuum to the velocity of light in the given medium. The determinations are usually made by measurement of the angle of emergence after the light passes from air through the liquid or solid and then through a glass prism and out into the air again. The refractive index may be calculated from the angle through which a telescope

must be turned in order to pick up the emerging beam on a cross-hair. The angle measured includes the refraction at the liquid-glass interface and at the glass-air interface, so that a calculation (shown in the appendix on page 661) is necessary to obtain the refractive index of the liquid against air. In some refractometers the angle of the emerging light beam is read on a scale which is calibrated directly in terms of the refractive index of the liquid against air since the refractive index of the prism glass is a constant. If desired, the ordinary refractive index measured in air may be converted into absolute refractive index by multiplying by the refractive index of air which is about 1.00029 at ordinary temperature. The refractive indices measured in air are the values usually recorded in tables.

The index of refraction depends on the wavelength of the light employed, the refraction for the red being less than that for the violet rays. Measurements of the refractive index are usually referred to the D-line of sodium 5893 Å. and are commonly designated by the symbol  $n_D$ . Sometimes the green mercury line at 5461 Å. or the lines of the hydrogen spectrum  $H_\alpha$ ,  $H_\beta$ , or  $H_\gamma$  are used as the source of light. Monochromatic light is used for the greatest precision but white light may be used if a compensating prism is adjusted so as to eliminate any color fringe. Because the angle of refraction changes with the wavelength to a different extent for each substance, it is necessary to adjust the compensator every time.

Measurements of refractive index are among the easiest and most accurate measurements of physical chemistry. They can be determined easily to two parts in 10,000. Careful control of temperature is necessary for accurate work.

The refractive indices of several different substances are given in Tables I and II.

TABLE I  
REFRACTIVE INDICES WITH DIFFERENT WAVELENGTHS OF LIGHT

Compound	Formula	$n_D^{20}$ *	$n_{H_\alpha}^{20}$	$n_{H_\beta}^{20}$	$n_{H_\gamma}^{20}$
Thenardite	$Na_2SO_4$	.....	1.464	1.474	1.485
Tridymite	$SiO_2$	.....	1.469	1.47	1.473
Formic acid	$CH_2O_2$	1.37137	1.36927	1.37643	1.38041
Ethyl bromide	$C_2H_5Br$	1.42386	1.42113	1.43046	1.43595
Benzene	$C_6H_6$	1.50144	1.49663	1.51327	1.52361
Aniline	$C_6H_7N$	1.58629	1.57948	1.60434	1.62074
<i>n</i> -Propyl alcohol	$C_3H_8O$	1.38543	1.38345	1.39008	1.39378
Nitrobenzene	$C_6H_5NO_2$	1.55291	1.54593	1.57124	.. . .

\* In refractive index the superscript specifies the temperature.

**Molar Refractions.** The refractive index of a fluid varies with temperature and pressure as the number of molecules in the path of the light is changed, but the *specific refraction*  $r$  is quite independent of these variables. On the basis of the electromagnetic theory of light, Lorenz and Lorentz have shown that

$$r = \frac{1}{d} \frac{n^2 - 1}{n^2 + 2} \quad [2]$$

where  $n$  is the refractive index and  $d$  the density. The *molar refraction* is equal to the specific refraction multiplied by the molecular weight.

*Example 1.* The refractive index  $n_D$  of allyl alcohol at  $20^\circ$  is 1.41345, the density at  $20^\circ$  is 0.8540, and the molecular weight is 58.078. Calculate the molar refraction.

$$\begin{aligned} Mr_D &= \frac{M (n^2 - 1)}{d (n^2 + 2)} = \frac{58.078 (1.41345^2 - 1)}{0.8540 (1.41345^2 + 2)} \\ &= \frac{58.078 \times 0.99784}{0.8540 \times 3.99784} = 16.97 \end{aligned}$$

The refractive index at  $20^\circ$ , the specific refraction, and molar refractions are given for several common liquids in Table II.

TABLE II  
MOLAR REFRACTIONS

Compound	Formula	$n_D^{20}$	$r_D^{20}$	$Mr_D^{20}$
Carbon tetrachloride	$\text{CCl}_4$	1.4573	0.1724	26.51
Acetone	$(\text{CH}_3)_2\text{CO}$	1.3571	0.2782	16.15
Benzene	$\text{C}_6\text{H}_6$	1.4979	0.3354	26.18
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	1.3590	0.2775	12.78
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	1.4929	0.2964	31.06
Chloroform	$\text{CHCl}_3$	1.4426	0.1823	21.40
Acetic acid	$\text{CH}_3\text{COOH}$	1.3698	0.2164	12.09
Ethyl acetate	$\text{CH}_3\text{COOC}_2\text{H}_5$	1.3701	0.2527	22.25
Water	$\text{H}_2\text{O}$	1.3328	0.2083	3.75

The refraction of light is an additive property, but it is also partly a constitutive property depending on the structural arrangement of the atoms within the molecule. The molecular refractions of a large number of organic and inorganic compounds have been determined and it has been found that many atoms and groups of atoms always contribute the same definite amount to the molecular refraction of any compound in which they are found. Thus in a homologous series

of aliphatic compounds a difference of  $\text{CH}_2$  in composition always produces a difference of 4.618 in the molecular refraction. The molecular refraction of hexane,  $\text{C}_6\text{H}_{14}$ , is 29.908, and by subtracting from this value six times the effect of the  $\text{CH}_2$  group, it is possible to obtain the atomic refraction of the hydrogen atom, namely, 1.100. Thus,

$$\frac{29.908 - (6 \times 4.618)}{2} = 1.100$$

From these data the atomic refraction of carbon is readily calculated thus

$$4.618 - (2 \times 1.100) = 2.418$$

Again the atomic refraction of bromine is obtained by subtracting the atomic refractions of two carbons and five hydrogens from the molecular refraction of ethyl bromide.

The atomic refractions are affected by the structural features. For example, the corrected molecular refraction of  $\text{BrH}_2\text{C}-\text{CH}_2\text{Br}$  is 26.966 and the corrected molecular refraction of  $\text{BrHC}=\text{CHBr}$  is 26.499.\* Subtracting the atomic refractions of the hydrogen and bromine atoms the value for  $\text{C}-\text{C}$  is 4.836 and for  $\text{C}=\text{C}$  it is 6.569. Since the two carbons together have a value of 4.836 it follows that a double bond between carbon atoms contributes an additional 1.733 to the molecular refraction.

Table III has been built up in the manner just indicated, averaging the results for a large number of compounds.

TABLE III  
ATOMIC REFRACTIONS

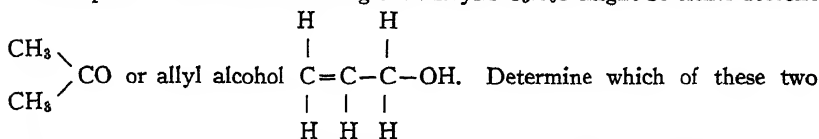
Group	$Mr_D$	Group	$Mr_D$
$\text{CH}_2$	4 618	Cl	5 967
H	1 100	Br	8 865
C	2.418	I	13 900
Double bond ( $\text{C}=\text{C}$ )	1.733	N (pri-amines)	2.322
Triple bond ( $\text{C}\equiv\text{C}$ )	2 398	N (sec-amines)	2.499
O (carbonyl)	2 211	N (tert-amines)	2.840
O (hydroxyl)	1.525	C N	5.459
O (ethers)	1.643		

This table is useful in determining the structure of molecules as it enables one to select the atom or group of atoms with the proper structural features so that the sum of the atomic refractions will add

\* The experimental values available in the literature give 27.0 and 26.3.

up to give a total which is equal to the experimentally determined molecular refraction.

*Example 2.* A substance having the analysis  $C_3H_6O$  might be either acetone



Determine which of these two substances it is from the fact that the molar refraction  $M_{rD}$  is 16.974.

Acetone		Allyl Alcohol	
3 carbons	= 7.254	3 carbons	= 7.254
6 hydrogens	= 6.600	6 hydrogens	= 6.600
1 carbonyl oxygen	= 2.211	1 double bond (C=C)	= 1.733
	<u>16.065</u>	1 hydroxyl oxygen	= 1.525
			<u>17.112</u>

Since the experimentally determined molar refraction agrees with that calculated for allyl alcohol, the substance is allyl alcohol rather than acetone.

Molar dispersions are differences between the molar refractions at different wavelengths. They are sometimes used instead of molar refractions because they are regarded as being connected with the molecular structure in a simpler manner.

**Rotation of Polarized Light.** Some materials, when placed in the path of a beam of polarized light, possess the property of rotating the plane of polarization to the right or left. Such substances are said to be optically active. The rotatory power of a substance is determined in a polarimeter, the principle of which is shown in Fig. 23.

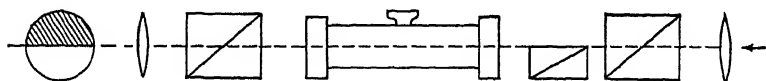


FIG. 23

A beam of monochromatic light is passed through a Nicol prism or other means for producing plane polarized light, thence through a tube containing the optically active material, and finally through a second Nicol prism. When these prisms are placed at right angles with no optically active material intervening, the only light passed by the first prism is stopped by the second and the rear field appears dark. When optically active material is introduced, however, the light appears again and the second prism must be rotated in order to prevent the passage of light. The number of degrees through which

the second prism must be rotated is a measure of the optical rotation. For dextrorotatory substances it is necessary to rotate the rear prism to the right; for levorotatory substances it must be turned to the left. Arrangements are made in the polarimeter with additional Nicol prisms so that the field of light is divided into two or three parts. A reading is made when the different parts match to give a uniform intensity over the whole area; such devices improve the accuracy of measurement.

The extent of the optical rotation depends on several factors, including the nature of the substance, the length of the column through which the light passes, the wavelength of the light, and the temperature. In solutions it depends also on the concentration of the solute. It is helpful then to define a term which will eliminate many of these variables. Thus

$$[\alpha]_t^\lambda = \frac{\alpha}{l(g/v)} = \frac{\alpha v}{lg} \quad [3]$$

where  $[\alpha]_t^\lambda$  is called the specific rotation,  $\alpha$  is the observed angle, and  $l$  the length in decimeters\*;  $t$  refers to the temperature of measurement and  $\lambda$  to the wavelength of the light. The yellow light of sodium, the D-line, is most frequently chosen. The green line of the mercury arc is also used. The concentration is expressed as  $g/v$  where  $g$  is the number of grams of optically active material in  $v$  milliliters of solution or liquid. The molar rotation is obtained by multiplying the specific rotation by the molecular weight of the dissolved material.† The specific rotations and molar rotations are used as an aid in determining the structure of the molecules and particularly as a rapid and accurate method of analysis. It is necessary to specify the solvent used, but it happens that the optical activity of many unionized liquids is unchanged by dissolving in water.

*Example 3.* An aqueous solution of maltose containing 13 g. in 100 ml. was examined in a polarimeter having a cell 20 cm. in length and found to have a rotation of  $34^\circ$ . What is the specific rotation of maltose? Another solution of maltose gave a rotation of  $42.5^\circ$  in a cell 10 cm. long. What is the concentration in grams per liter?

$$[\alpha]^D = \frac{34 \times 100}{2 \times 13} = 130.8^\circ$$

$$g = \frac{42.5 \times 1000}{1 \times 130.8} = 325$$

\* It would be preferable to express the length in centimeters as is usually done with other physical chemical properties but the older tables all use decimeters.

† In the older literature these molar rotations are divided by 100.



**Optical Activity and Chemical Structure.** Optical activity is found most often in compounds containing an asymmetric carbon atom, that is, a carbon atom which is attached to four different atoms or groups of atoms. One of the simplest examples is lactic acid. Two different optical isomers are possible, dextro- and levo-lactic acid, as shown in Fig. 24.

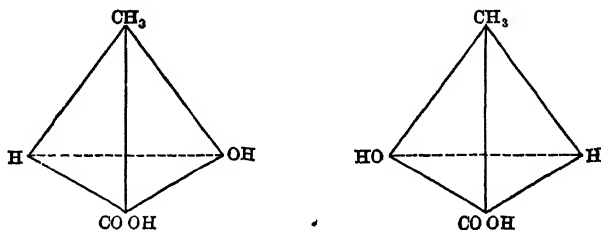


FIG. 24

They are practically identical in their properties except that they rotate the plane of polarized light in opposite directions. When lactic acid, or other material containing an asymmetric carbon atom, is synthesized in the laboratory, a mixture containing equal parts of each form is produced. Such a mixture is called *racemic*. It may be separated into its optical isomers by forming derivatives with optically active bases, usually alkaloids, which have different solubilities. In a second method one or the other isomer is destroyed by microorganisms. For example, if the mold *Penicillium glaucum* is introduced into a solution of racemic tartaric acid, it will thrive at the expense of the dextro acid and leave the pure levo form. In a third method the two isomers are allowed to crystallize in different forms which are then separated by hand picking. Again, it has been found possible to decompose preferentially one component of a racemic mixture through the use of circularly polarized ultraviolet light.

The magnitude of the rotation is in part connected with the relative masses of the atoms or groups of atoms surrounding the central asymmetric carbon atom, and some regularities occur in homologous series. The specific rotation of some solutes is the same in different solvents, but usually it varies in a manner which is specific for each solvent and solute. Apparently some loose combination with the solvent at certain parts of the molecule changes the rotation. Ionization of the optically active molecule usually leads to a marked change in the specific rotation. Optical activity is not restricted to the asymmetric carbon atom; it has been observed in compounds containing asymmetric atoms of nitrogen, sulfur, tin, cobalt, and others. More-

over, it has been observed in certain types of organic compounds which contain an unsymmetrical grouping but no asymmetric atom.

Crystals sometimes exhibit optical rotation which may be explained in two different ways. Quartz, for example, rotates the plane of polarized light by virtue of the spiral arrangement of units in the crystal lattice, whereas certain other types of crystals rotate the light because the molecules themselves are optically active. The proof that crystals of tartaric acid with "right-handed faces" give a solution which is dextrorotatory and that "left-handed faces" give solutions which are levorotatory constituted one of the brilliant researches of Louis Pasteur.

**Absorption of Light.** The mechanism by which light is absorbed by molecules will be discussed more fully in Chapters XIX and XX but it may be stated here that absorption of light in the visible and ultraviolet regions of the spectrum involves the displacement of electrons within the molecules. Absorption in the infrared region where the wavelengths are longer involves the displacement of atoms. According to the quantum theory a beam of light is composed of many units of radiation called photons. The energy of one photon is called a quantum of energy and it depends on the wavelength of the light, the quantum being larger in the ultraviolet, of lesser energy in the blue, and still less in the red and infrared. However, all the photons in monochromatic light of a given wavelength have the same energy.

There are only certain displacements of electrons or atoms within the molecule which are permissible according to the quantum theory, and when the quanta in a beam of light passing through a given material happen to have about the same energy as the energy required to bring about a permissible change within the molecule there is a definite probability that the photon will be stopped and its energy consumed in effecting the displacement inside the molecule.

When polychromatic light containing many different wavelengths is passed into a substance some of the light may be absorbed, the rest being either transmitted or reflected. A substance appears colored because part of the light is absorbed. For example, a solution of copper ions appears blue because when white light is passed through it, the red and yellow light is absorbed and only the blue is transmitted to the eye. The colored light, transmitted or reflected, can be measured by passing it through a spectrometer and spreading it out into a spectrum by means of a prism or grating. The bright lines are images of the slit of the spectrometer. When the light extends over a considerable range of wavelengths the corresponding section of the

spectrum is continuous. Dark regions in the spectrum show that light corresponding to those particular wavelengths is absorbed. An examination of the character and intensity of the absorption spectrum is a method widely used for the identification and determination of the absorbing material.

Absorption in the ultraviolet is measured with the photographic plate; absorption in the visible is readily detected either with the eye or with a photographic plate.\* Infrared radiation does not affect the eye, or the common photographic plate, or the ordinary photoelectric cell, and so the absorption spectrum is determined with a sensitive thermopile which absorbs the heat rays and converts them into electricity which is measured with a galvanometer. Near infrared radiation can be measured with specially sensitized photographic plates. Glass prisms and lenses are satisfactory for visible light, whereas quartz is generally used for the ultraviolet, and rock salt or potassium bromide for the infrared. The apparatus must be transparent to whatever light is being used.

The wavelength of light is measured in Ångström units. One Ångström,† Å., is one hundred millionth ( $10^{-8}$ ) of a centimeter.

Light is described also in *wave numbers* which are expressed in reciprocal centimeters. For example, ultraviolet light of 2500 Å., has a wavelength of  $2.5 \times 10^{-5}$  cm. and a wave number of  $1/(2.5 \times 10^{-5})$  or 40,000 reciprocal centimeters. Strictly speaking, the wavelengths used in calculating wave numbers should be measured in vacuum:

The *frequency* of light, obtained by multiplying the wave number by the velocity of light, is important in photochemistry (page 580) and in energy calculations.

The percentage of light transmitted at a given wavelength may be measured in several different ways. The spectrum may be photographed in a spectrograph and the blackening of the plate at each wavelength gives an indication of the amount of light transmitted. In this way it is easy to determine at what wavelengths absorption bands occur. The plate is calibrated by comparing it with a spectrum of known wavelengths, such as the mercury or iron spectrum, taken with the same spectrograph.

Over a limited range of exposure the blackening is directly proportional to the amount of light striking the plate. The blackness may be compared directly with an adjacent exposure on the same

\* Apparatus and methods of spectrometry are described in "Experimental Physical Chemistry" by Daniels, Mathews, and Williams, pages 39-43 and 58-67.

† The millimicron,  $m\mu$ , which is  $10^{-7}$  cm., is a unit of wavelength equal to 10 Å. General practice is tending toward its elimination.

plate produced in the same length of time by a beam of light whose intensity has been reduced by a definite, measured amount using a sector wheel, a Nicol prism, or a wire screen. Also the density of the spectrogram may be determined quantitatively by passing a narrow beam of light along the plate and measuring with the help of a photoelectric cell or thermopile the light absorbed by different parts of the plate.

The use of photocells in absorption measurements is increasing rapidly in popularity. The deflection of a sensitive galvanometer connected to a photoelectric cell or photovoltaic cell is directly proportional to the light transmitted and it is not necessary to make a photograph of the spectrum. The light may be divided into short spectral regions by means of filters or by prisms or gratings, and the per cent transmission determined for a narrow band of the spectrum.

The principle of such an instrument is shown in Fig. 25. A beam of light is passed through a narrow slit onto an optical grating *A*, from which it is reflected through a cell *C* containing the solution, and thence to the photocell *D* which is connected to the galvanometer. The percentage of light transmitted is calculated by dividing this deflection

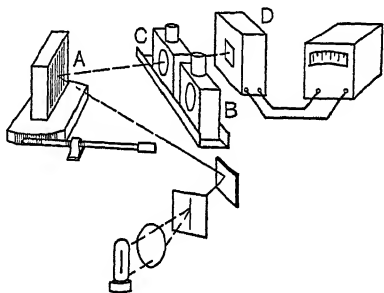


FIG. 25

by the deflection  $I_0$ , obtained when cell *B* containing the solvent is slid along into the path of the light, displacing the cell *C*. By turning the screw the grating is turned so as to pass any desired wavelength through the cell. In this way the transmission  $I/I_0$  may be determined for the different wavelengths and the spectrum may be mapped. When the desired absorption band is located the instrument may be set for this wavelength and the transmission determined for different concentrations of absorbing material. The positions of the absorption bands and lines serve for identification and criteria of purity whereas the percentage transmissions serve for quantitative analyses.

Emission spectra of volatilized metals and compounds are readily obtained using an arc, a spark, or a flame, and these are valuable in qualitative and quantitative analysis. In quantitative estimation of the amounts of material, it is necessary to compare the blackening of the plate with the blackening produced by known amounts of the standard substance volatilized and activated under identical conditions of current and voltage.

**Lambert's Law.** It was stated that the extent of the absorption depends on the probability that the energy of the quantum will be transferred to the molecule where it can effect a chemical reaction or where it is dissipated eventually as heat. It depends also on the number of molecules in the path of the light. This probability is expressed mathematically by the proportionality constant  $k'$  in the formula

$$\frac{dI}{I} = -k'dl \quad [4]$$

where  $I$  is the intensity of light, i.e., the number of quanta per second per square centimeter hitting the surface, and  $dI$  is the change in light intensity produced by absorption in a very thin layer  $dl$  of the absorbing material. A large value of this proportionality constant  $k'$ , indicates that the material is very absorbing. The value of  $k'$  varies with the wavelength of light.

At a given wavelength the intensity  $I$  of transmitted light after the beam has passed through  $l$  centimeters of the absorbing medium is related to the initial intensity  $I_0$  by equation (5) which is obtained by integrating\* equation (4) between the limits  $I_0$  when  $l = 0$ , and  $I$  at length  $l$ .

$$\ln \dagger \frac{I}{I_0} = -k'l \quad [5]$$

**Beer's Law.** The intensity of transmitted light is affected by a change in the concentration of absorbing material as well as by a change in the thickness of the absorbing material. If the length of the absorbing cell is fixed, Beer's law gives the relation

$$\frac{dI}{I} = -k''dc \quad [6]$$

where  $c$  is the concentration, often expressed in moles per liter. Usually equations (4) and (6) are combined giving the Beer-Lambert law

$$\ln \frac{I}{I_0} = -klc$$

or in exponential form

$$I = I_0 e^{-klc} \quad [7]$$

where  $k$  is called the *absorption coefficient*.

\* Details of this simple integration are given in Daniels' "Mathematical Preparation for Physical Chemistry," p. 132.

†  $\ln$  signifies  $\log_e$ ;  $\log$  signifies  $\log_{10}$ .

The equation is such that a straight line is produced when the logarithm of the fraction of light transmitted,  $I/I_0$ , is plotted against the concentration of absorbing material when the same absorption cell is used so that the length  $l$  is constant.

Equation (7) may be written with logarithms to the base 10, as

$$\log \frac{I}{I_0} = -Elc \quad [8]$$

where  $E$  is known as the *extinction coefficient*.

**Example 4.** Using a 1.9-cm. absorption cell, the absorption of blue light by bromine dissolved in carbon tetrachloride was found to be as follows:

Concentration of $\text{Br}_2$ ( $c$ ) in moles per liter	0.00546	0.00350	0.00210	0.00125	0.00066
Transmission ( $I/I_0$ )	0.010	0.050	0.160	0.343	0.570

Calculate the absorption coefficient.

In **Fig. 26**,  $\log I/I_0$  is plotted against concentration and the constant  $k$  is calculated from the slope of the line to be 448.

What per cent of the incident light would be transmitted by 2 cm. of a solution containing 0.00155 mole of bromine per liter of carbon tetrachloride?

$$\log \frac{I}{I_0} = -\frac{k l c}{2.303} = -\frac{448 \times 2 \times 0.00155}{2.303} = -0.603 = \bar{1}.397$$

$$\frac{I}{I_0} = 0.25$$

That is, 25 per cent of the light is transmitted and 75 per cent is absorbed, neglecting the amount reflected.

The amount of light absorbed,  $A$ , is equal to the difference between the incident light and the transmitted light. Thus

$$A = I_0 - I = I_0(1 - e^{-kcl}) \quad [9]$$

In this calculation the reflected light is ignored, but it may be calculated. It amounts to about 4 per cent when a perpendicular beam of light goes from air to glass or glass to air.

The absorption of light is widely used now for measuring quickly and accurately the concentration of a colored material.

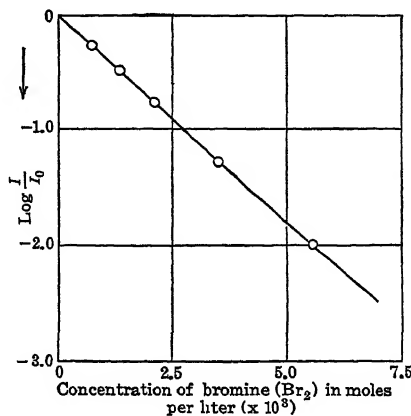


FIG. 26

The transmission of light can be measured visually by comparing the intensity with the intensity of light after passing through a known standard solution in a colorimeter.

In a colorimeter the depth of a known standard solution is adjusted until the intensity of transmitted light just matches, according to the eye, the intensity transmitted by the unknown solution being analyzed. The concentration is readily calculated from the depth of the solutions and the concentrations of the standard solution.

Analysis by the absorption of light has many advantages. It is quick and accurate and can be carried out without disturbing the material or withdrawing a sample. Whereas it is limited to colored substances it must be remembered that most substances are colored in the ultraviolet and infrared. Applications in these fields are beginning to receive attention.

**Absorption and Chemical Constitution.** The absorption of light may be used for determining not only the concentration of the colored substance but also for identifying it. The spectroscope is very widely used for analysis by emission spectra, but it is used also for absorption spectra. Many ions, dyes, and other colored organic and inorganic substances have characteristic absorption spectra. A ketone group ( $=C=O$ ), for example, absorbs between 3000 and 4000 Å., depending on the adjacent groups, and again in the infrared at 58,000 Å.

The absorption of light by a solution changes with the thickness of the layer and with the concentration in a manner which is characteristic for each absorbing material. Sometimes the spectrum is photographed at a number of different thicknesses or at a number of different concentrations and the region of absorption gradually narrows as the solution is diluted. The wavelength of the last part of the absorption band to fade out is characteristic of the absorbing material.

It is often possible to predict the absorption spectra of organic compounds from a knowledge of the structure and the influence of substituted groups. Likewise the absorption spectra are helpful in deciding questions of chemical constitution. Several spectra, plotted in different ways, are shown in Figs. 27, 28, and 29.

In Fig. 27 are shown the results of several spectragrams of an 0.001 *N* solution of sulfanilic acid starting with a column 50 mm. thick and diminishing the thickness by successive differences of 5 mm. The logarithms of these thicknesses were then plotted against the wave number at which the absorption band fades out.

Figure 28 gives an excellent absorption spectrum of chlorophyll from green leaves showing the two components, chlorophyll A and chlorophyll B, with slightly different absorption maxima. This spectrum

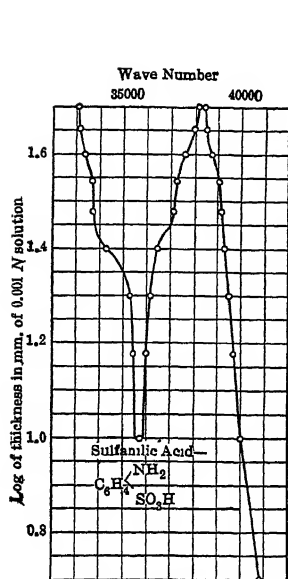


FIG. 27

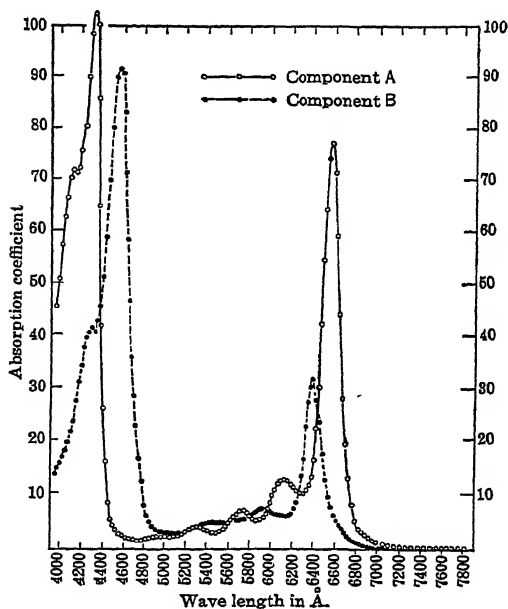
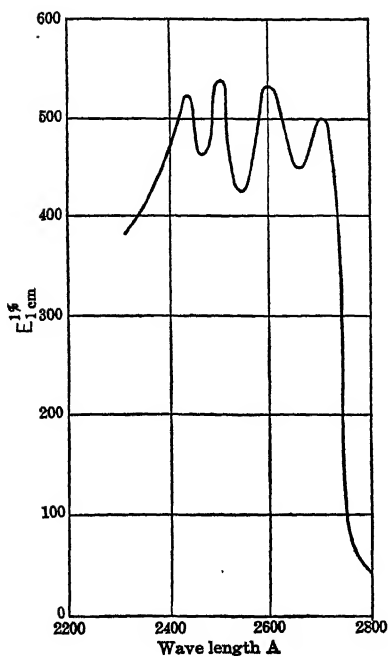
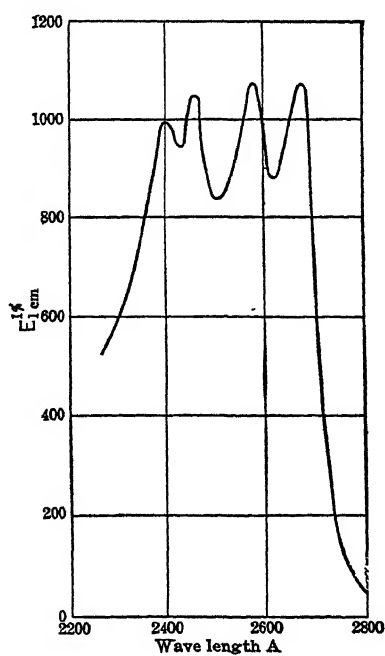


FIG. 28



(a)



(b)

FIG. 29



is adapted from one by Zcheile\* obtained with a spectrometer provided with a photoelectric cell.

Figures 29*a* and *b* are taken from an investigation on vitamins by Ewing, Vandenbelt, and Kamm.† The absorption spectrum of vitamin K<sub>1</sub> obtained from biological sources and dissolved in hexane is shown in Fig. 29*a*. Several different pure organic compounds suspected of being the effective vitamins were then examined in the same spectrograph, but only the compound 2, 3-dimethyl-1, 4-naphthoquinone gave a spectrum closely resembling that of the vitamin. The similarity of the spectrum of this compound, shown in Fig. 29*b*, to that of the vitamin was instrumental in showing that this compound is vitamin K<sub>1</sub>. Then biological tests proved that this deduction was correct. The curves in Fig. 29*a* and *b* are given as extinction coefficients *E* at different wavelengths in Ångströms, using a 1 per cent solution in hexane in a cell 1 cm. thick. The smaller absorption in Fig. 29*a* shows that the vitamin was not completely pure.

**The Parachor.** It has been shown that the refraction, rotation, and absorption of light are easily measurable quantities which are useful in deciding questions of molecular structure. The determination of density may be used also. The molar volumes of organic liquids at their critical temperatures, i.e., at the temperature at which a liquid is undistinguishable from the corresponding gas at high pressures as explained on page 23, should offer possibilities for significant comparison. When the gram-molecular weights of different substances are taken it is clear that the comparison involves equal numbers of molecules. It has been found that the volume of atoms and groups of atoms in organic compounds at their boiling points have roughly the same values from compound to compound so that the molar volumes at the boiling point can be approximated by taking the sum of the atomic volumes. There is some basis for this relation because it will be shown on page 162 that the boiling points of nonpolar liquids come at roughly equal fractions of the critical temperatures.

Very much more accurate results are obtained, however, if the molar volumes are compared not at their boiling points under atmospheric pressures but at temperatures at which the liquids have the same surface tension. Sugden‡ discovered a relationship which, based partly on this idea and partly on a relation pointed out by McLeod, shows that the surface tensions of many liquids are propor-

\* Zcheile, *J. Phys. Chem.*, **38**, 95 (1934).

† Ewing, Vandenbelt, and Kamm, *J. Biol. Chem.*, **131**, 345 (1939).

‡ Sugden, *J. Chem. Soc.*, **125**, 1177 (1924); "The Parachor and Valency," George Routledge and Sons, London, 1930.

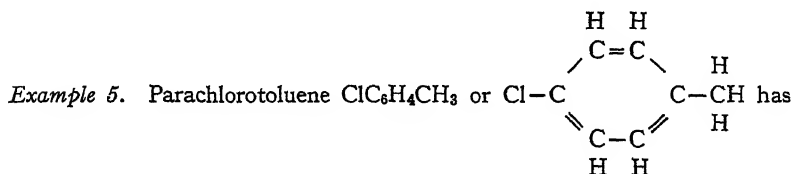
tional to the fourth power of the difference between the densities of the liquid and vapor. According to this relation the molecular parachor  $P$  is defined as follows

$$P = \frac{M}{D - d} \gamma^{\frac{1}{4}} \quad [10]$$

where  $\gamma$  is the surface tension defined on page 163,  $M$  is the molecular weight,  $D$  is the density of the liquid, and  $d$  is the density of the saturated vapor, all measured at the same temperature. The density of the vapor may be neglected when the vapor pressure is low. The molar parachor  $P$  is the sum of the atomic parachors, just as the molar refraction is equal to the sum of the atomic refractions, and the values for the atomic values are obtained in a similar manner by averaging many different molar values and taking differences. In the molar parachors the structural features play a part so that the physical measurements can be used in helping to decide questions of molecular structure. A summary of the values is given in Table IV.

TABLE IV  
ATOMIC AND STRUCTURAL PARACHORS

C	4.8	Br	68.0	Double bond	23.2
H	17.1	I	91.0	Triple bond	46.6
O	20.0	N	12.5	5-membered ring	8.5
Cl	54.3	S	48.2	6-membered ring	6.1



a surface tension of 32.24 dynes per centimeter at 25°. Its density at this temperature is 1.065.

Neglecting the density of the vapor at this temperature, what is the value of the parachor?

$$P = \frac{M}{D - d} \gamma^{\frac{1}{4}} = \frac{126.5}{1.065} (32.24)^{\frac{1}{4}} = 283$$

What is the value calculated from the atomic and structural parachors?

$$P_{\text{calc}} = 54.3 + (7 \times 4.8) + (7 \times 17.1) + (3 \times 23.2) + (1 \times 6.1) = 283.3$$

The parachor seems to give quite accurate results in correlating structure with the physical properties of organic compounds.\*

\* Quayle, Owen, and Estes, *J. Am. Chem. Soc.*, **60**, 2716 (1938); also later papers.

**Electron Diffraction.\*** The arrangements of building units within crystals have been clearly revealed by means of the diffraction of x rays, as already described. A beam of electrons generated in a vacuum between two charged plates (as in a radio tube) has many of the properties of a beam of light of very short wavelength (page 573). These electrons, when moving at high uniform velocities, are deflected by the nuclei of atoms, and the extent of the deflections permits a calculation of the arrangement of atoms and the distance between the atomic nuclei. Space models are constructed which account for the observed deflections in a manner similar to that by which space models are constructed for interpreting the Laue photographs obtained from the diffraction of x rays. More direct methods of interpretation are also available.†

The x rays are very penetrating; the electron beams are but slightly penetrating. The x rays, then, are suitable for studying the structure of crystals and solids and liquids, but the electron diffraction is more suitable for studying gases and adsorbed gases and surface layers. The arrangement of atoms and ions in the crystals determines the crystal lattice, whereas the arrangement and distance of atoms in the individual molecules of a material in the gas phase give the molecular structure. This determination of the distance and angles between atoms in a molecule is now finding important applications in the calculation of chemical equilibria and reaction rates and in many other fields.

In carrying out measurements on molecular structure the electrons at a very uniform voltage of about 40,000 volts in a vacuum are shot out of a small pinhole at a photographic plate about 10 cm. away. A stream of vapor of the substance to be studied is passed at a low pressure ( $10^{-5}$  mm.) across this space. Short exposures of about a second each and subsequent development of the plate give rings of varying intensity depending on the positions of atoms within the molecule. The diameters of the rings of different intensities are measured and used to decide which of many possible spatial arrangements of the atoms is the correct one.

Figure 30 is reproduced from an electron diffraction photograph of hexamethylbenzene prepared by Dr. A. J. Stosick of the Gates Chemical Laboratory of the California Institute of Technology.

One other example of the use of these diffraction patterns in molecular structure may be cited. Chemical evidence shows that in

\* Brockway, *Rev. Modern Phys.*, **8**, 231-266 (1936); Clark and Wolthuis, *J. Chem. Educ.*, **15**, 64-74 (1938).

† Pauling and Brockway, *J. Am. Chem. Soc.*, **57**, 2684 (1935).

1, 2-dichloroethylene the two carbon atoms are joined by a double bond with one hydrogen and one chlorine atom attached to each carbon. If it is assumed that all the atoms lie in a plane, there are two possibilities: in the *cis* form the two chlorine atoms lie on the same side of the carbon double bond; and in the *trans* form they lie on opposite sides. The distances between the two chlorine atoms will be different in the two forms. Electron diffraction patterns show that in the *cis* isomer of dichloroethylene the distance is 3.22 Å., and in the *trans* isomer it is 4.27 Å. Models of these two molecules are shown in Fig. 35 and the

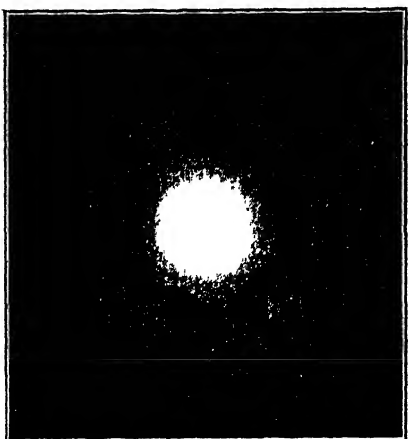


FIG. 30

radii of some of the common elements of organic chemistry as determined by electron diffraction are given in Table VI on page 83.

**Dipole Moments.** Nonpolar or electrically symmetrical molecules tend to give nearly perfect gases or ideal solutions, with properties which are proportional to the mole fractions. The simple laws of physical chemistry involving surface tensions, heats of vaporization and solution, additive volumes, and other phenomena apply much better to the nonpolar substances than to the polar. Thus, polar or electrically dissymmetrical molecules form gases which are not ideal and liquids which are associated. Any description of their properties in solutions is complicated.

Molecules are composed of positively and negatively charged particles in such numbers that they are neutral as a whole. In polar molecules there is a finite distance of separation between what may be termed the centers of gravity of the positive and negative electricity, and the polarity of a molecule becomes less as these centers of gravity in a molecule approach each other. When placed in an electrical field a polar molecule will tend to orient itself in such a way that the positive part of the molecule points toward the negative electrode and the negative part points to the positive electrode. The force required to orient the molecule will depend on the magnitude of the charges and on the distance between them. The *dipole moment*  $\mu$  is defined as the product of one of the charges and the distance between the two average centers of positive and negative electricity. It serves

as a useful quantitative measure of the extent to which a molecule is polar.

Experimental measurements of this dipole moment have become of great importance in studying the structure of molecules because they measure the electrical dissymmetry in molecules. Thus they provide information concerning the shape of a molecule. Moreover, solubility and the properties of solutions, the deviations from simple gas laws and ideal solutions, and the influence of solvents on reaction rates and equilibrium constants probably can be interpreted more quantitatively through measurements of dipole moments.

The measurement of the dipole moment is complicated by the fact that all molecules, whether polar or nonpolar, possess the property of becoming polarized when placed in an electrical field. Even those nonpolar molecules whose electrical charges are uniformly distributed, as in  $\text{H}_2$  or  $\text{CCl}_4$ , acquire a positive charge at the part which is nearest the negative electrode and a negative charge at the part which is closest to the positive electrode. This induced dipole is sometimes called distortion polarization  $P_D$ , while the other, permanent polarization is called orientation polarization  $P_\mu$ . The latter quantity is the more significant in physical chemistry. It can be determined from measurements of dielectric constants in two different ways — by determining the dielectric constant in the gaseous state at several temperatures, or by determining the dielectric constant contribution of a solute in dilute solutions in a nonpolar solvent and extrapolating to infinite dilution. Under this condition the molecules are so far apart that they do not induce electrical charges in each other. The first method is more accurate and simple in theoretical treatment but less convenient in experimental procedure. The quantitative relations follow.

The *dielectric constant*  $\epsilon$  measures the relative effect of the medium on the force with which two oppositely charged plates attract each other. The dielectric constant of a vacuum is taken as unity, but for practical purposes the dielectric constant of air is nearly unity. The dielectric constant of a liquid or gas is determined\* readily by measuring the electrical capacity of a condenser when empty and when filled. The force attracting the two plates of the condenser depends on the size of the plates, the distance between the plates, the medium between them, and the quantity of electricity which they hold. In the same condenser the size and distance of the plates are constant, and the ratio

\* "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1941. Chapters XIII and XXV.

of forces, i.e., the dielectric constant  $\epsilon$ , is equal to the ratio of charges of electricity. Then

$$\epsilon = \frac{C_z}{C_{\text{air}}} \quad [11]$$

where  $C_z$  and  $C_{\text{air}}$  refer to the electrical capacities of the condenser when filled with the medium and with air.

The Clausius-Mosotti equation may be developed on the basis of theories of electrical charges induced by charged plates. It can be written approximately as follows and used to define  $P$  in terms of  $\epsilon$ :

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} \quad [12]$$

where  $P$  is the molar polarization,  $M$  is the molecular weight, and  $d$  is the density in grams per cubic centimeter. The dielectric constant  $\epsilon$  is simply a ratio, and  $M/d$  is the molar volume of the material. The constant  $P$  then is expressed in terms of a molar volume.

The total molar polarization is due to two effects as already explained, thus

$$P = P_D + P_\mu$$

Debye showed how these two quantities can be separated. The induced polarization  $P_D$  is unaffected by an increase in temperature but the orientation polarization  $P_\mu$  depends on temperature because the random thermal agitation tends to break up the alignment of the molecules, and at the higher temperatures more of the permanent dipoles which would tend to orient themselves with respect to each other are torn apart.

The orientation polarization and the dipole moment can then be determined as shown by Debye\* thus

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = P_D + P_\mu = \left(\frac{4}{3} \pi N\right) \alpha + \left(\frac{4}{3} \pi N\right) \frac{\mu^2}{3kT} \quad [13]$$

where  $N$  is the Avogadro number  $6.02 \times 10^{23}$ ,  $\alpha$  is the polarizability or electrical moment per molecule induced by an electrical field of unit strength,  $\mu$  is the permanent dipole moment, and  $k$  is the Boltzmann constant or the gas constant per molecule,† defined as follows:

$$k = \frac{R}{N} = \frac{8.314 \times 10^7}{6.02 \times 10^{23}} = 1.38 \times 10^{-16} \text{ erg per degree}$$

\* Debye, "Polar Molecules," Chemical Catalog Co., New York, 1929.

† When different quantities as  $P$ ,  $\mu$ , and  $k$  are to be combined they must all be expressed in the same system of units — preferably c.g.s. units, giving ergs.

The factor  $\frac{4}{3}\pi N$  is used in electrodynamics to convert these molecular quantities into molar quantities.

In the gaseous state the molecules are so far apart that they do not induce electrical effects in adjacent molecules and  $\alpha$  and  $\mu$  may be considered constants. Then equation (13) gives a straight line

$$P = a + b \frac{1}{T} \quad [14]$$

when  $P$  is plotted against the reciprocal of the absolute temperature. The molar polarization  $P$  of the gas at a given temperature is obtained from the dielectric constant  $\epsilon$  at that temperature by using formula (12). The dipole moment  $\mu$  is then obtained from the slope  $b$  of the straight line

$$\mu = \sqrt{\frac{9kb}{4\pi N}} = 0.01282 \times 10^{-18} \sqrt{b} \quad [15]$$

These calculations are illustrated in Fig. 31 for the chlorine-substituted compounds of methane as measured by Sanger.\* It is seen

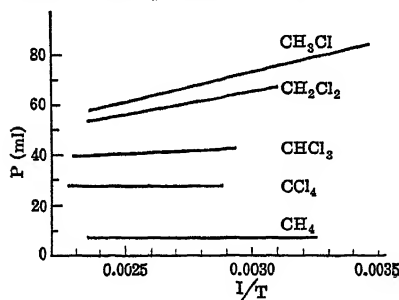


FIG. 31

that CH<sub>4</sub> and CCl<sub>4</sub> give horizontal lines when  $P$  is plotted against  $1/T$ . The slope is zero, and the dipole moment is zero. This is to be expected because the molecules are symmetrical. The sloping lines for CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and CH<sub>3</sub>Cl show that the molecules have dipole moments due to the unsymmetrical arrangement of the negative chlorine

atoms. The steeper the slope the greater is the dipole moment.

According to another method the molar polarization of the solute in a nonpolar solvent is extrapolated to infinite dilution. If at infinite dilution  $P_D$  is equal to  $\frac{n^2 - 1}{n^2 + 2} \frac{M}{d}$ , where  $n$  is refractive index of solute,

$$P_\mu = P - \frac{n^2 - 1}{n^2 + 2} \frac{M}{d} \quad [16]$$

Since

$$P_\mu = \frac{4}{9} \frac{\pi N \mu^2}{kT}$$

$$\mu = 0.01282 \times 10^{-18} \sqrt{P_\mu T} \quad [17]$$

Dipole moments of several typical substances are given in Table V. The dipole moment is always of the order of  $10^{-18}$  electrostatic unit.

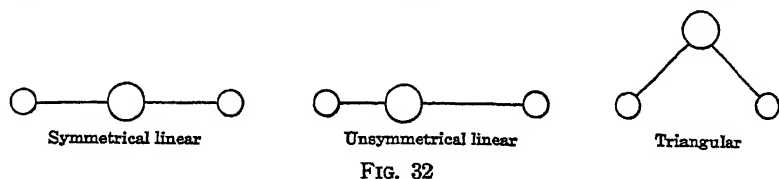
\* Sanger, *Physik. Z.*, **27**, 562 (1926).

This is to be expected because the unitary charge of electricity is  $4.8 \times 10^{-10}$  electrostatic unit (page 657) and the diameter of most molecules is of the order of  $10^{-8}$  cm. The dipole moment is the product of the charge and the distance between the two charges. Dipole moments are sometimes expressed in Debye units, one such unit being  $10^{-18}$  electrostatic unit.

TABLE V  
DIPOLE MOMENTS  
(In electrostatic units)

AgClO <sub>4</sub>	$4.7 \times 10^{-18}$	C <sub>6</sub> H <sub>5</sub> Cl	1.73	HCl	1.03
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	4.23	C <sub>6</sub> H <sub>5</sub> OH	1.70	HBr	0.79
(CH <sub>3</sub> ) <sub>2</sub> CO	2.8	C <sub>2</sub> H <sub>5</sub> OH	1.70	HI	0.30
H <sub>2</sub> O	1.84	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	1.56	N <sub>2</sub> O	0.14
CH <sub>4</sub>	0	H <sub>2</sub> S	1.10	CO	0.12
CH <sub>3</sub> Cl	1.86	H <sub>2</sub>	0	CS <sub>2</sub>	0
CH <sub>2</sub> Cl <sub>2</sub>	1.59	N <sub>2</sub>	0	C <sub>2</sub> H <sub>4</sub>	0
CHCl <sub>3</sub>	1.15	Cl <sub>2</sub>	0	C <sub>2</sub> H <sub>6</sub>	0
CCl <sub>4</sub>	0	CO <sub>2</sub>	0	C <sub>6</sub> H <sub>6</sub>	0

Carbon dioxide and water might have structures corresponding to a symmetrical linear molecule, to an unsymmetrical linear molecule, or to a triangle as shown in Fig. 32. The dipole moments recorded in Table V show that carbon dioxide has zero moment and the molecule



must be symmetrical and linear. If it were unsymmetrical or triangular there would be an unbalancing of the electrical charges. On the other hand, water has a pronounced dipole moment and it cannot have the symmetrical, linear structure. Measurements of band spectra show that it has the triangular form rather than the unsymmetrical linear form.

To a certain extent dipole moments of groups of atoms may be added as vectors in molecules, but there are deviations which are important aids in determining the molecular structure.\*

\* Additional examples of the use of dipole moments are given by Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931.

Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933, pages 138-198.



The *cis* and *trans* isomers of dichloroethylene have been discussed already in connection with electron diffraction. Measurements of dipole moments are also significant. The *cis* isomer with the two chlorines on one side of the carbon-carbon double bond has a dipole moment of  $1.56 \times 10^{-18}$ , whereas the more symmetrical *trans* isomer has a dipole moment of nearly zero.

The disubstituted benzenes, shown in Fig. 33 are interesting. The arrows indicate the vectors and show that the dipole moment increases progressively as the molecule becomes more unsymmetrical.

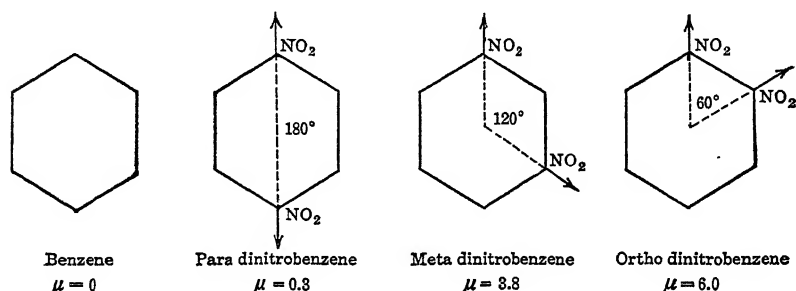


FIG. 33

**Atomic Models.** The distance between atoms may be determined from measurements of electron diffraction. The "bond angles" which valence bonds make inside the molecule may be found from measurements of dipole moments. These considerations apply best to the nonpolar compounds or covalent molecules in which atoms are held together chiefly by electron pairs rather than by electrostatic attraction.

By measuring the interatomic distances in many nonpolar compounds Pauling has been able to assign bond lengths or atomic radii to each element on the assumption that these bond lengths are additive. Not only is the atomic radius fixed for a given atom but also the bond angles are fixed. These rules hold as long as the bonds are normal and the molecule is free from strain. Table VI gives the bond radii for a number of atomic species.

The single bond of carbon has a bonding radius of  $0.77 \text{ \AA}$ , and hydrogen has a bonding radius of  $0.30 \text{ \AA}$ , so the separation for C-H is  $0.30 + 0.77 = 1.07 \text{ \AA}$ . Similarly, the interatomic distance for C-C is  $0.77 + 0.77 = 1.54 \text{ \AA}$ . When double bonds are present all the adjacent bonds lie in a single plane. Thus ethylene and benzene have planar structures.

TABLE VI

## BOND RADII

Hydrogen	0.30 Å.	Nitrogen (nitrate) (single)	0.70 Å.
Carbon (single bond)	0.77	Chlorine	0.99
Carbon (double bond)	0.67	Bromine	1.14
Carbon (triple bond)	0.60	Iodine	1.33
Oxygen (single bond)	0.66	Nitrogen (cyanide)	0.55
Oxygen (double bond)	0.57	Carbon (benzene) (C—C)	0.69
Nitrogen (amino)	0.70	Carbon (benzene) (C—H)	0.77
Nitrogen (nitrate) (double)	0.65		

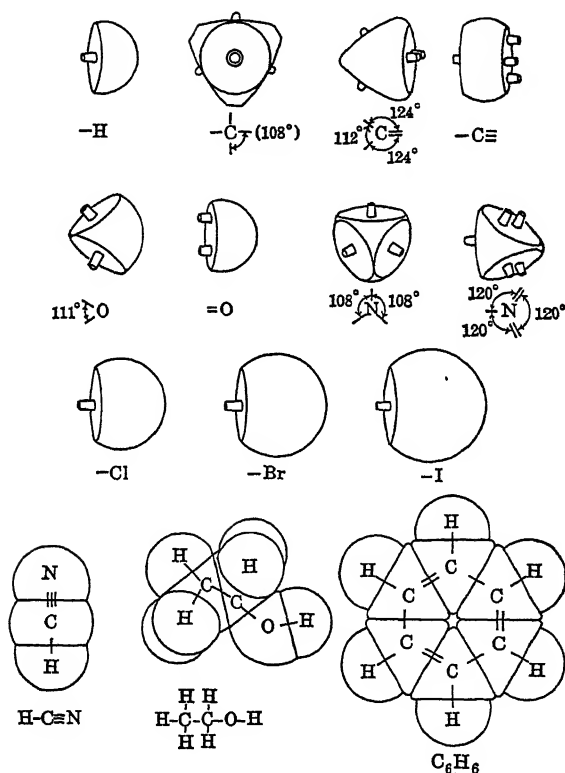


FIG. 34

These bond radii and bond angles are represented pictorially in Fig. 34. Models are available\* in which 1 in. represents 1 Å. and the faces of the atoms are cut so as to give the correct bond angles. Models of molecules may then be built up which represent the actual relations

\* Fischer-Hirschfelder atomic models.

on a large scale and certain deductions can be drawn from these models. Models are shown in Fig. 34 for hydrocyanic acid, ethanol, and benzene.

In Fig. 35 the *cis* and *trans* forms of dichloroethylene are shown and the reasons for the difference in dipole moments is readily apparent. The symmetrical *trans*-form has a dipole moment of 0.3 whereas the

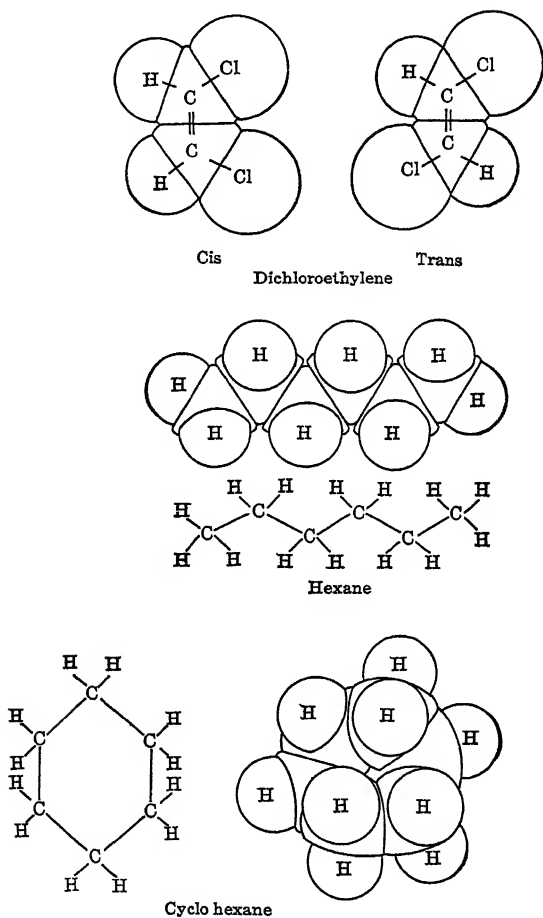


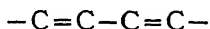
FIG. 35

unsymmetrical *cis*-form has considerably larger dipole moment of 1.56.

Hexane, which is shown also in Fig. 35, has a long snakelike structure which can move around in various positions, but the probabilities of free motions of the cyclohexane shown just below it are greatly

reduced. This reduction of the probable motions leads to a decrease in entropy, which will be discussed on page 130.

Whenever the interatomic distance is not equal to the sum of the bond radii it may be concluded that there is something abnormal about the structure, such as a strained position or the existence of more than one structure. For example, *resonance* is said to exist when more than one configuration is possible, so that electrons can move back and forth with great rapidity to occupy both positions. Such molecules have properties of both configurations. Conjugated double bonds are good examples of such resonating structures. Butadiene, for example, has the structure



and illustrates this type of resonance. It is found that in butadiene the carbon-carbon distances are not exactly equal to the sum of the normal bond radii. When resonance occurs the compounds are more stable than would otherwise be expected and they have abnormally low heats of reaction.

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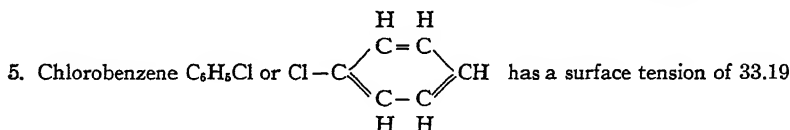
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#### PROBLEMS

1. For propionic acid  $d = 1.0158$  and  $n = 1.3953$ . (a) Calculate the molar refraction, and (b) compare it with the sum of the atomic refractions (propionic acid has the formula  $C_2H_5COOH$ ). *Ans.* (a) 17.49; (b) 17.59.
2. Geraniol has the formula  $C_{10}H_{18}O$  and its chemical behavior is such as to warrant the conclusion that it is a primary alcohol. The value of  $n_D$  is 1.4745 from which the molecular refraction is calculated to be 48.71. What conclusions can you draw regarding the structure of this compound? *Ans.* Two double bonds.
3. The specific rotation  $\alpha_D$  of a solution of *d*-ethoxysuccinic acid in water is 33.02 at 17°C. Calculate the concentration of this compound in grams per liter in a solution which has a rotation of 2.02° when measured in a polarimeter at 17°C. in which the container of the solution is 20 cm. long. *Ans.* 30.6 g. per l.
4. When a solution of 6.0  $\mu$ g. of vitamin A in 1 ml. of chloroform was placed in a standard-sized cell and treated with a standard amount of antimony trichloride

solution in chloroform, a blue color was produced which transmitted 60 per cent of the incident light as indicated by the galvanometer of a photoelectric colorimeter. A solution of the vitamin of unknown concentration transmitted 38.0 per cent of the incident light under the same conditions. Calculate the concentration of the vitamin in micrograms ( $\mu\text{g}$ ) of vitamin A per milliliter, assuming that Beer's law holds.

*Ans.* 11.4  $\mu\text{g}$ . per ml.



dynes per cm. at  $25^\circ$ . Its density at this temperature is 1.106.

(a) Neglecting the density of the vapor at this temperature, what is the value of the parachor?

(b) What is the value calculated from the atomic and structural parachors?

*Ans.* (a) 244.1. (b) 244.3.

6. The dielectric constants and densities of germanium tetrachloride at various temperatures are tabulated. Calculate the molar polarizations at these temperatures, and determine the dipole moment.

*Ans.* Zero.

$t^\circ$	0	20	30	40	50
$\epsilon$	2.491	2.443	2.417	2.395	2.370
$d$	1.9226	1.8762	1.8533	1.8296	1.8063

7. By extrapolation the molar polarization of pyridine oxide,  $\text{C}_5\text{H}_5\text{NO}$ , in an infinitely dilute solution in dioxane is found to be 411 at  $25^\circ$ . The molar refraction of  $\text{C}_5\text{H}_5\text{NO}$  is 28. Calculate the dipole moment.

*Ans.*  $4.33 \times 10^{-18}$ .

8. Calculate the molar refraction of diethyl ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ . The refractive index,  $n_D$  at  $17.1^\circ$  is 1.35424, and the density at  $17.1^\circ$  is 0.7183 g. per ml. Compare this value with the sum of the atomic refractions.

*Ans.* (a) 22.34 (b) 22.32.

9. Calculate what concentration of bromine in a layer 10 cm. thick will be necessary to absorb 50 per cent of the blue light passing through it.

10. In order to test the validity of Beer's law in the determination of vitamin A, solutions of known concentration were prepared and treated by a standard procedure with antimony trichloride in chloroform to produce a blue color. The per cent transmission of the incident filtered light for each concentration is as follows:

Conc. Micrograms per Milliliter	Per Cent Transmission
1.0	66.8
2.0	44.7
3.0	29.2
4.0	19.9
5.0	13.3

Determine whether or not Beer's law applies to this solution.

11. A solution of *l*-mandelic acid in water containing 1.56 g. in 100 ml. rotated polarized light  $4.91^\circ$  in a polarimeter which had a cell 20 cm. long. The D-line of sodium was used as a light source. Calculate the specific rotation.

12. At  $35^\circ$  the surface tension of butyl laurate ( $\text{C}_{11}\text{H}_{23}\text{COOC}_4\text{H}_9$ ) is 27.47 dynes per cm. The density is 0.8490. Calculate the parachor of the compound, assuming

that the density of the vapor is negligible, and compare it with the value calculated from the atomic parachors.

13. The following data for a sample of linseed oil at 25° were found experimentally. Refractive index,  $n_D$ , = 1.4792; density = 0.9260; molecular weight,  $M$ , = 783 (polymerized); dielectric constant,  $\epsilon$ , = 2.349 extrapolated to infinite dilution in benzene. Calculate the dipole moment of the linseed oil at 25°.

14. Calculate from the atomic refractions, the refractive index of allyl acetate,  $n_D$ , at 20°. The density of allyl acetate at 20° is 0.9276. The formula is  $\text{CH}_3\text{COOCH}_2\text{CH}=\text{CH}_2$ . The experimental value is 1.4045.

15. It has been established that the refractive index of a solution of carbon tetrachloride in benzene is a linear function of the mole fraction of either component. For benzene,  $n_D^{18} = 1.5024$ . For carbon tetrachloride,  $n_D^{18} = 1.4618$ . Calculate the per cent by weight of  $\text{CCl}_4$  in a solution of the two having a refractive index at 18° of 1.4807. The term mole fraction is defined on page 174.

16. A preparation of *L*-proline when dissolved in water gave a concentration of 25 g. per liter at 20° and rotated polarized light from the D-line of sodium through  $-3.05^\circ$ , as measured with a polarimeter in a cell 20 cm. long. The specific rotation at 20° of pure *L*-proline is  $-84.9^\circ$ . What conclusions can be drawn as to the purity of the product?

17. A 10-cm. length of a certain 1-molar solution absorbs 68 per cent of monochromatic blue light (4800 Å.) which passes through it. What is the absorption coefficient of this solution for this wavelength? What percentage of light of this wavelength will be absorbed in passing through 30 cm. of this solution?

18. At 30°, the density of boron triethyl  $\text{B}(\text{C}_2\text{H}_5)_3$  is 0.6774, and its surface tension is 19.84 dynes per cm. Using the atomic parachors of carbon and hydrogen, calculate the atomic parachor of boron.

19. The molar polarization  $P$  of ammonia varies with temperature as follows:

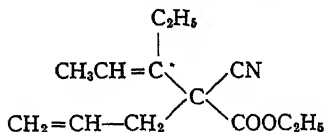
$t$ (°C.)	19.1	35.9	59.9	113.9	139.9	172.9
$P$ (ml.)	57.57	55.01	51.22	44.99	42.51	39.59

(a) Plot  $P$  against  $1/T$  and determine the dipole moment of ammonia.

(b) If the density of ammonia gas at 59.9° and 1 atm. is 0.632 g. per liter (0.000632 g. per ml.), what is the dielectric constant of ammonia under these conditions?

20. The molar polarization of silicobromoforn  $\text{SiHBr}_3$  is 46 at 25°. The induced electrical moment,  $\alpha$ , may be taken as  $1.308 \times 10^{-28}$ . Calculate the dipole moment of this molecule.

21. In synthesizing ethyl (*l*-ethyl propenyl) allylcynoacetate,



none of whose physical constants were known, a product was obtained having a refractive index,  $n_D^{25}$ , of 1.4617 and a density of 0.9704 at 25°. What conclusions can be drawn as to the purity of the compound?

22. Nicotine is examined in a tube 10 cm. long, at  $25^\circ$  with the sodium D line.  $\alpha_D^{25} = -162^\circ$ ;  $d_{25} = 1.099$ . Calculate the percentage of error in the value of  $\alpha$  caused by (a) an error of  $0.1^\circ$  in the angle, (b) an error of 0.1 mm. in tube length, and (c) an error of 0.01 in density.

23. Using Beer's law and Lambert's law, derive the formula for the use of the colorimeter,  $c_x = \frac{d_s}{d_x} c_s$ , where  $c$  and  $d$  stand for the concentrations and depths,  $s$  refers to the standard solution, and  $x$  refers to the unknown solution.

## CHAPTER V

### HEAT, WORK, AND HEAT CAPACITY

**Thermodynamics.** The quantitative relations between heat and other forms of energy are studied in the science of thermodynamics. They are important because all other forms of energy tend to change into heat, and the quantitative measure of this tendency leads to important physical and chemical relations. The laws of thermodynamics are exact because they are based on the statistical behavior of large numbers of molecules and because they are not concerned with the time variable, which complicates many physical and chemical phenomena.

Thermodynamics has been used in physics for a century, and it has found extensive applications in engineering; but its practical application in chemistry is a comparatively recent development. The present chapter provides an introduction to the simple concepts of heat and work. It is followed by a chapter on heat measurements in chemical reactions and then by a chapter on the more abstract concepts of thermodynamics. Throughout the study of solutions and chemical equilibria, these concepts will be applied to correlate and explain the observed facts. Applications of practical importance are given in the chapter on Chemical Thermodynamics (page 517).

**Energy.** Energy may be stored in a given system by virtue of position as, for example, a stone above the earth's surface, or a spring under compression, or by virtue of chemical properties due to the arrangement of atoms and electrons within a molecule. Energy may also exist in other forms such as the kinetic energy of a moving ball or molecule.

This energy may be released, under the proper conditions, to do work: to push a piston in an engine cylinder or to send a current of electricity through the windings of an electric motor. The energy may be converted into heat, thus raising the temperature of the system itself or of the surroundings. Energy, work, and heat are all expressed in the same units: calories, joules, or ergs.

Although symbols are employed to represent the total energy stored in a system, it should be borne in mind that usually it is not necessary to know this energy in absolute terms. When a process occurs



in which the energy of a system undergoes change, our measurements merely give the gain or loss in the energy of the system as a result of the change. For example, if a body having a mass of 1 g. falls, under the influence of gravity, through a distance of 1 m., the resulting loss in potential energy is  $1 \text{ g.} \times 980.7 \text{ cm./sec.}^2 \times 100 \text{ cm.} = 98,070 \text{ ergs.}^*$  In this calculation, the absolute values of the potential energy of the body in its initial and final states are not involved; it is known only that in the final state the body possesses 98,070 ergs less potential energy than it possessed in its initial state. The potential energy is converted into kinetic energy, and this in turn is converted into heat when the falling object is suddenly stopped.

Energy may be expressed as the product of two factors — an intensity factor and a capacity factor. Examples are given in Table I.

TABLE I

INTENSITY AND CAPACITY FACTORS OF ENERGY INVOLVED IN VARIOUS PROCESSES

Energy	Intensity	Capacity
Mechanical (ergs)	Force (dynes)	Change in distance (cm.)
Kinetic (ergs)	Change in $\frac{1}{2}$ velocity <sup>a</sup> (cm. per sec.) <sup>2</sup>	Mass (g.)
Surface (ergs)	Surface tension (dynes per cm.)	Change in area (sq. cm.)
Volume expansion (ergs)	Pressure (dynes per sq. cm.)	Change in volume (cm. <sup>3</sup> )
Heat (calories)	Difference in temperature (degrees)	Heat capacity (calories per degree)
Electrical (joules)	Difference in potential (volts)	Coulombs (amperes $\times$ seconds)

It is evident that the different energies may be compared but that no relation exists between the intensity factors alone or between the capacity factors alone. For example, electrical energy may be converted quantitatively into heat energy, but the rise in temperature cannot be calculated from the voltage unless the number of coulombs and the heat capacity of the system are known. It is clear also that the same quantity of energy may be generated by a small quantity of water passing through a turbine from a great height as from a large quantity of water falling through a short distance.

\* It will be remembered that in the c.g.s. system a dyne is a force which gives to a mass of 1 g. an acceleration of 1 cm. per sec. per sec. An erg is the energy produced by 1 dyne acting through 1 cm. The force of gravity is about 980.7 dynes, depending slightly on the latitude and the elevation above sea level.

**The First Law of Thermodynamics.** The first law is merely a statement of the principle of the conservation of energy, according to which energy cannot be created or destroyed. In other words, *the sum of all the energies in an isolated system remains constant*. This fundamental principle was first clearly formulated by Mayer in 1842, shortly after the publication of important investigations by Helmholtz, Joule, and others on the transformation of work into heat and heat into work. Subsequently, many exact experiments have proved conclusively that mechanical work may be transformed completely into heat. In some of these experiments a measured amount of work was used in stirring a liquid while the rise in temperature was measured, and in others a known quantity of electricity was passed through a heating coil of known resistance immersed in a liquid containing a thermometer.

Throughout this book the "calorie" will be defined arbitrarily as equal to 4.1833 international joules, in agreement with the practice of many American physical chemists.\*

Our confidence in the first law of thermodynamics rests largely on the fact that no exceptions to it have yet been found. At first sight one might think that the energy expended in lifting a piece of iron is destroyed if the iron is dissolved in sulfuric acid, but the iron in the resulting ferrous sulfate is at a higher level and possesses potential energy equal to the energy expended in the lifting. If energy is expended in coiling a steel spring and the spring is dissolved in acid, the energy appears to be lost; but more heat is evolved by a coiled spring than by an uncoiled spring. The energy is immediately distributed throughout all the molecules of the solution. The difference is so small, however, that it has not been detected by present calorimetric methods.

Even the new developments in nuclear chemistry do not contradict the first law; for according to the theory of relativity, matter is a form of energy, and the large evolution of energy produced by reactions between atomic nuclei in transmutation experiments (page 607) is offset by the actual decrease in mass. Einstein showed that

$$1 \text{ g.} = 9 \times 10^{20} \text{ ergs} \quad [1]$$

The proportionality factor  $9 \times 10^{20}$  is the square of the velocity of

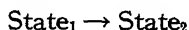
\* The 15° calorie (i.e., the heat required to raise 1 g. of water from 15 to 16°) is equivalent to  $4.1855 \pm 0.0008$  absolute joules according to the best determinations. Many of these values will have to be changed in the future as apparatus is improved and more accurate measurements are made. A table of physical constants and their values is given on page 657.

light expressed in centimeters per second. It is evident that the law of the conservation of energy and the law of the conservation of mass are essentially the same and that no violation of thermodynamics occurs when matter is converted into energy, or energy into matter. However, these changes can be brought about only in reactions involving atomic nuclei and with enormous energies such as are present in hot stars or in electrical apparatus producing a million volts and more. Nuclear changes are not involved in ordinary chemical and physical phenomena.

A change in the energy of a system will be brought about if the system gives or receives work, or if it absorbs or evolves heat. The *work* is designated by  $w$ . A positive sign indicates that the work is done by the system on its surroundings and a negative sign shows that the system is having work done on it, as for example, when a gas is compressed by the applications of external pressure. The *heat* exchange is designated by  $q$ ;  $+q$  for heat absorbed by the system and  $-q$  for heat evolved.

In *chemical* thermodynamics we are not ordinarily interested in the energy which a system has by virtue of its distance from the center of the earth or by virtue of any movement of the system through space. We are interested in the *internal energy*,  $E$ , of which chemical energy is an important manifestation. The absolute value of the internal energy depends on many complicated factors such as molecular, atomic, and electronic motions, which are not readily determined, but a change in internal energy, designated by  $\Delta E$ , can be readily measured by physical chemical methods.

The symbol  $\Delta$  always indicates a change, and in physical chemistry it refers to the difference between the values of a property in the initial and the final states. For example, if  $E_1$  represents the internal energy in the initial state and  $E_2$  the internal energy in the final state, in the reaction



Then

$$\Delta E = E_2 - E_1$$

The initial state is taken as the state which happens to be written down at the left of a chemical equation and the final state is designated as the state written at the right. This convention applies to any chemical or physical change.

Since energy can neither be created nor destroyed it follows that the internal energy of the final state must be equal to the internal energy of the initial state plus the energy added\* in the form of heat or any

\*If heat is removed  $q$  is given a negative sign.

kind of work. Then

$$E_2 = E_1 + (q - w)$$

or

$$E_2 - E_1 = \Delta E = q - w \quad [2]$$

This equation may be regarded as a mathematical formulation of the first law of thermodynamics.

If there is no change of internal energy, as in the isothermal expansion of a perfect gas, the work done must be exactly equal to the heat absorbed. Again, if there is a chemical reaction and the internal energy of the system decreases, i.e.,  $E_2$  is less than  $E_1$ , the released energy may appear as heat evolved and work done. Nothing is stated regarding the relative amounts of heat and work but the two taken together ( $q - w$ ) must be equal to the change in internal energy. Under special conditions it is possible to have either  $q$  or  $w$  or both equal to zero.

For infinitesimal changes equation (2) is written

$$dE = dq - dw \quad [3]$$

but there is an important reservation which must be made regarding the use of  $dq$  and  $dw$ . Changes in internal energy  $E$  like changes in pressure or volume depend only on the initial and final state and are independent of the intermediate stages. Mathematically they may be classed as perfect differentials, and

$$\int dE = E_2 - E_1 = \Delta E$$

On the other hand,  $q$  and  $w$  do not represent differences between initial and final states. They refer to processes rather than states, and their values depend on the manner in which the change is carried out. The terms  $dq$  and  $dw$  are not perfect differentials and their integrals should not be written as the differences between initial and final values (e.g., as  $q_2 - q_1$ ) but simply as  $q$  or  $w$ .

**Reversible Processes.** *Vaporization of a Liquid.* When a gas increases in volume it pushes back the surrounding atmosphere and does work. Imagine that a liquid is placed in a cylinder provided with a weightless, frictionless piston and that it is set into a large reservoir at the boiling point of the liquid. The fact that no machine can be built with a weightless, frictionless piston in no way affects the conclusions drawn from this idealized process. The vapor pressure of the liquid at this temperature is exactly equal to the atmospheric pressure, and the whole system is in a state of equilibrium. If now the temperature of the reservoir is raised by an infinitesimal amount the vapor

pressure of the liquid will be slightly greater and the piston will be pushed back against the atmospheric pressure. As more liquid evaporates, the volume increases, and the pressure in the cylinder is thus maintained constant; heat flows in from the reservoir to maintain the temperature constant and offset the cooling caused by vaporization.

The work done is the product of the resisting pressure and the increase in volume. The increase in volume is the distance through which the piston is driven out multiplied by the cross-sectional area of the piston. If the liquid in the cylinder is water, the temperature will be  $100^\circ$ , and when 1 mole has been evaporated the increase in volume can be calculated on the assumption that the vapor behaves as an ideal gas and that the volume of the liquid (0.018 liter) is negligible:

$$w = p \Delta V = 1 \times (22.41 \times 373.1/273.1) = 30.6 \text{ liter-atm.}$$

Since it is assumed that the ideal gas laws are obeyed,  $RT$  may be substituted for  $p \Delta V$ . Then

$$w = RT = 0.08206 \times 373.1 = 30.6 \text{ liter-atm.}$$

or

$$w = RT = 1.987 \times 373.1 = 741.3 \text{ cal.}$$

The work done in this process depends only on the temperature and is independent of the cross section of the piston or the pressure or volume. In very exact work it is not legitimate to consider a vapor at its boiling point as a perfect gas, and then the volume change must be measured experimentally or calculated with more exact equations of state.

The energy consumed in doing this external pressure-volume work comes from heat absorbed from the reservoir by the evaporating liquid. A great deal more energy is absorbed, however, in separating the molecules from their neighboring molecules in the liquid. To vaporize a gram of water at  $373.1^\circ \text{ K.}$  and atmospheric pressure 539 cal. is required. This corresponds to  $18.02 \times 539$  or 9713 cal. per mole. Then under these conditions of constant pressure the total heat absorbed is equal to the sum of the two quantities as given by equation (4).

$$q = \Delta E + w = \Delta E + p \Delta V \quad [4]$$

Since  $q = 9713$  and  $p \Delta V = 741$ , the change in internal energy  $\Delta E$  must be 8972 calories.

This process of absorbing heat and doing external work is reversible in the example just given because at any time the vaporization can be

stopped by decreasing the temperature by an infinitesimal amount or by increasing the pressure slightly, thus making internal and external pressures exactly equal. Increasing the pressure still further by an infinitesimal amount causes the vapor to condense and give back the heat of vaporization to the reservoir. A *reversible process*, then, is defined as one which may be reversed at will by making infinitesimal changes.

After a mole of water has been evaporated by decreasing the pressure it can be condensed again by increasing the pressure, and thus the whole system may be restored to its original condition. Such a process, which involves a series of changes and restores the system to its original condition, is called a *cycle*. A *reversible cycle* is one which is carried out by applying infinitesimal changes under conditions such that the system is at all times practically in a state of equilibrium.

**Isothermal and Adiabatic Expansion.** When a gas expands against an external pressure, it does work. If the gas is compressed, then a certain amount of energy must be consumed in doing work on the gas. When the gas expands its temperature falls, unless an amount of heat is supplied from its surroundings to compensate for the energy expended in the performance of external work. When the temperature is maintained constant by compensating with heat, the process is said to be *isothermal*. On the other hand, when a gas undergoes expansion or compression and it neither receives heat from nor imparts heat to its surroundings, the process is known as an *adiabatic* process. If a gas is compressed adiabatically, the temperature rises and tends to cause the gas to expand. This temperature effect causes the pressure to rise more rapidly than in isothermal compression; and therefore, more work is required to bring about a given decrease in volume by adiabatic compression than by isothermal compression. This becomes clear if we make use of the diagram shown in Fig. 36, in which pressures are plotted as ordinates and volumes as abscissas. If a gas is compressed isothermally from volume  $v_1$  to volume  $v_2$ , the work done will be represented by the area  $ABv_2v_1$ , whereas if it is compressed adiabatically, the work done will be represented by the larger area  $ACv_2v_1$ . It will be noticed that the slope of the adiabatic line,  $AC$ , is steeper than that of the isothermal line,  $AB$ .

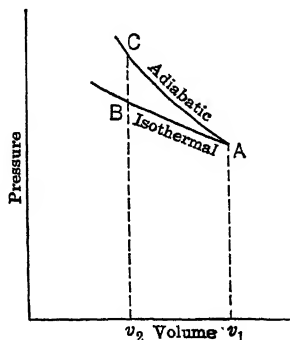


FIG. 36

**Maximum Work by Isothermal Expansion.** The maximum work which can be done by the *isothermal expansion* of a perfect gas is an important quantity in theoretical chemistry. Imagine a gas enclosed in a cylinder fitted with a frictionless and weightless piston and placed in a thermostat at the temperature  $T$ . The external pressure on the piston is decreased by a small amount,  $-\Delta p$ , and the gas expands by an amount  $\Delta v$ . In this expansion the pressure of the gas in the cylinder decreases until it becomes equal to the external pressure, and then the piston ceases to rise. This process differs from the one described previously on page 93 where the gas was in contact with *liquid* at its boiling point so that the pressure in the cylinder was maintained constant. A second decrease in pressure produces a second expansion  $\Delta v$ , and as the pressure is decreased in successive amounts the volume undergoes a series of expansions. In each little expansion the work done is the external pressure multiplied by  $\Delta v$ , and the total work done in expanding from the *initial* volume  $v_1$  to the *final* volume  $v_2$  is equal to the sum of the work done in each expansion.

The maximum work is obtained when the  $\Delta v$ 's are made infinitesimally small, and under these conditions the exact value is readily obtained by integral calculus,\* thus

$$w_{\max} = \int_{v_1}^{v_2} p \, dv \quad [5]$$

Only if the work done is maximum work can sufficient energy be stored to reverse the process, compressing the gas and restoring the original conditions. Under the conditions of maximum work the internal pressure can be substituted for the external or resisting pressure because the two can never differ by more than an infinitesimal amount,  $dp$ , and the system is then always practically in a state of equilibrium; that is, it is a reversible process.

If 1 mole of a perfect gas is taken,  $pV = RT$ , or  $p = \frac{RT}{V}$ , and

$$w_{\max} = \int_{v_1}^{v_2} \frac{RT}{V} \, dV$$

Since  $R$  and  $T$  are constants, integration gives

$$w_{\max} = RT \int_{v_1}^{v_2} V^{-1} \, dV = RT \ln \frac{V_2}{V_1} = RT \, 2.303 \log \frac{V_2}{V_1} \quad [6]^\dagger$$

\* The significance of this equation may be found in Daniels, "Mathematical Preparation for Physical Chemistry," pages 162-164.

† The more general equation for  $n$  moles of perfect gas is  $w_{\max} = nRT \, 2.303 \log v_2/v_1$ . The capital  $V$  is used for 1 mole.

The maximum work done by a gas in expansion is equal to the minimum work required to compress the gas, and the calculation is made by simply interchanging the limits of integration and using the smaller volume for the upper limit. In integrations, the upper limit always refers to the final state and the lower limit refers to the initial state. The signs then take care of themselves. The negative value obtained for  $w$  in compression means that work is done on the gas.

*Example 1.* What is the maximum work which can be obtained by the isothermal expansion of 1 mole of a perfect gas at  $0^\circ$  from 2.24 liters to 22.4 liters?

$$w_{\max} = 2.303RT \log \frac{V_2}{V_1} = 2.303 \times 1.987 \times 273.1 \times \log 10 = 1250 \text{ cal.}$$

Then 1250 cal. is also the minimum amount of work required to compress the gas from 22.4 to 2.24 liters at  $0^\circ$ .

The maximum work for 1 mole of gas may be calculated in terms of pressures instead of volumes since  $p_1 V_1 = p_2 V_2$  and  $V_2/V_1 = p_1/p_2$ . Then

$$w_{\max} = RT \ln \frac{p_1}{p_2} = -RT 2.303 \log \frac{p_2}{p_1}$$

**Absorption of Heat.** In problems for which the first law of thermodynamics, equation (2), is most often used, the only work done is pressure-volume work, i.e.,  $dw = p dv$ . In the special case where there is no volume change,  $dv$  is zero and  $w$  is therefore zero. Then for processes in which the volume is kept constant and no electrical or other work is done

$$q_v^* = \Delta E + 0 = \Delta E \quad [7]$$

In particular, the heat of reaction, measured under conditions of constant volume, is equal to the change in internal energy. According to this equation if no outside work is done the heat evolved,  $-q_v$ , is equal to the decrease in the internal or chemical energy.

Constant-pressure processes are generally more common in chemistry than the constant-volume processes because most operations are carried out in open vessels. It is convenient then to use another quantity which involves pressure and volume.

*Heat content*†  $H$  is such a quantity. It is defined by the equation

$$H = E + pV \quad [8]$$

\* A subscript below a quantity indicates that the property indicated by the subscript is kept constant, thus  $q_v$  shows that the process is restricted to constant volume.

† The term heat content will be used in this book following the Lewis and Randall system. The term enthalpy is used by some authors for the expression  $E + pV$ .



Changes in heat content rather than absolute values are important in chemistry and

$$\Delta H = \Delta E + \Delta(pV) \quad [9]$$

The change in heat content can be visualized readily under the special condition of constant pressure as equal to the increase in internal energy plus the pressure-volume work of expansion or compression.

$$\Delta H = \Delta E + P \Delta V \quad (\text{at constant pressure}) \quad [10]$$

Under this condition of constant-pressure equation (4) becomes

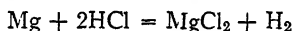
$$q_p = \Delta E + p \Delta V$$

Substituting the equivalent of  $\Delta H$  in equation (10)

$$q_p = \Delta H \quad [11]$$

In other words, the heat absorbed in a process at constant pressure is equal to the increase in heat content.

*Example 2.* One mole of magnesium is dissolved in an excess of hydrochloric acid at 25° in (a) an open beaker and (b) a closed bomb. The heat of the reaction, at constant pressure,  $q_p$ , is -110,130 cal. What is the heat of reaction at constant volume,  $q_v$ ?



$$q_p = q_v + p \Delta v = q_v + \Delta n RT$$

where  $\Delta n$  = the increase in the number of moles of gas.

$$q_v = -110,130 - 1 \times 1.987 \times 298.1 = -110,722 \text{ cal.}$$

At constant pressure the evolution of heat is less than the heat of reaction at constant volume by the amount of energy required to do the external work, of pushing out one mole of hydrogen gas against the atmospheric pressure, namely, 592 cal. It is to be noted that the final state is not the same in the two reactions, the hydrogen occupying a larger volume in the first. It is assumed that the internal energy of the products is independent of the pressure.

*Example 3.* Show that the work done by the liberation of a mole of a perfect gas in a reaction at constant pressure and temperature is independent of the pressure of the gas and independent of the cross section of the vessel in which it is liberated. The work done is given by the relation

$$w = p \Delta V$$

If the pressure is reduced to half an atmosphere the volume will be twice as large, and the product  $\frac{1}{2}p \times 2\Delta V$  will be the same. Likewise if the cross section of the cylinder and piston is doubled the displacement of the piston for a given evolution of gas will be halved and  $\Delta V$  will remain unchanged.

**Heat Capacity.** Heat can be absorbed not only in physical and chemical changes but also by simply raising the temperature.

*Heat capacity*,  $c$ , is defined as the ratio of the heat absorbed to the rise in temperature for a small increase in temperature. When the absorption of heat is carried out under a condition of constant volume the molar heat capacity is

$$C_v = \frac{dq_v}{dT} \quad [12]$$

Molar quantities are usually designated by capital letters. The molar heat capacity at constant pressure is

$$C_p = \frac{dq_p}{dT} \quad [13]$$

Substituting for  $dq_v$  and  $dq_p$  their values in terms of  $dE$  and  $dH$  and indicating the restriction imposed by partial differentials, (appendix, page 662),

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v \quad [14]$$

and

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad [15]$$

If the heat capacity is determined at constant volume no external work is done, and the heat absorbed is a measure of the increase in internal energy of the system. A greater amount of heat is absorbed at constant pressure.

Any two of the three variables, temperature, pressure, and volume, suffice to define the condition of a substance if  $E$  is a function only of  $T$ ,  $p$ , and  $v$ . The change in the internal energy of a mole of gas may, therefore, be expressed by the fundamental equation of partial differentiation

$$dE = \left( \frac{\partial E}{\partial T} \right)_v dT + \left( \frac{\partial E}{\partial V} \right)_T dV \quad [16]$$

where temperature and volume are the variables chosen. The derivative  $\left( \frac{\partial E}{\partial T} \right)_v$  represents the heat absorbed per degree by the gas at constant volume and, therefore, according to equation (14), it may be replaced by  $C_v$ . Equation (16) now assumes the form

$$dE = C_v dT + \left( \frac{\partial E}{\partial V} \right)_T dV \quad [17]$$

But since  $dE = dq - dw$ ,

$$dq = C_v dT + \left( \frac{\partial E}{\partial V} \right)_T dV + dw$$

The work done when the volume of a mole of gas, liquid, or solid increases by an amount  $dV$  at pressure  $p$  is  $p dV$ . Hence

$$dq_p = C_v dT + \left( \frac{\partial E}{\partial V} \right)_T dV + p dV$$

This equation means in words that the heat absorbed when a substance is heated slightly at constant pressure is equal to the sum of three quantities: (1) the temperature increase multiplied by the heat capacity at constant volume; (2) the volume increase multiplied by the rate at which the internal energy increases with volume, all other factors being held constant; (3) the work done in expansion.

Further examples of the use of partial differentiation in thermodynamics are given in the appendix on page 662.

**Internal Energy of Gases.** In order to determine whether a gas undergoes any change in temperature when it expands into a vacuum, Gay-Lussac, in 1807, carried out the experiment indicated in Fig. 37.

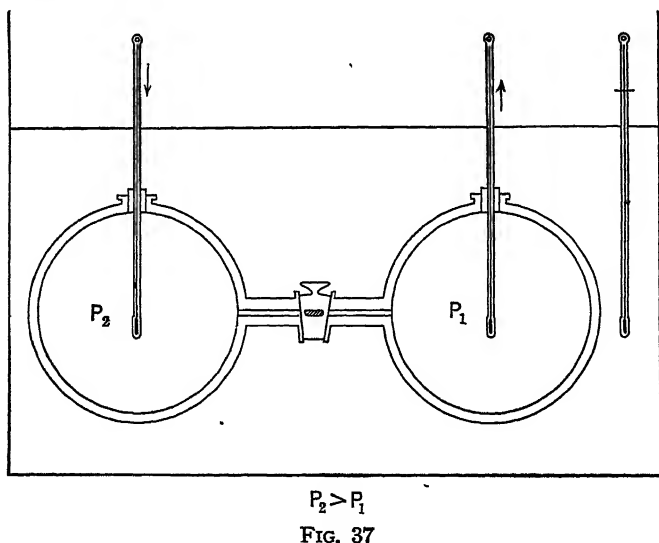


FIG. 37

Two large vessels of equal capacity were provided with thermometers and were connected by a stopcock. The vessel at the left was filled with gas, and the other evacuated. On opening the valve and allowing the gas to expand into the evacuated vessel, the temperature of the

gas in the vessel at the left ( $P_2$ ) was observed to fall. A corresponding rise in temperature occurred in the other vessel ( $P_1$ ), owing to the compression by the inflowing gas. When equilibrium of pressure had been established, the decrease of temperature in the first vessel was found to be exactly equal to the increase of temperature in the second vessel. From this, Gay-Lussac concluded that, taken as a whole, the gas showed no tendency to become warmer, or colder, during free expansion. A somewhat similar experiment was performed by Joule in 1844. He immersed two similarly connected vessels in a calorimeter, and found that no appreciable change in the temperature of the water of the calorimeter occurred during the free expansion of a gas, as the heating in one vessel was offset by the cooling in the other.

From these two experiments it is evident that, when a perfect gas expands freely into a vacuum, heat is neither evolved nor absorbed. Furthermore, the volume of the system as a whole remains constant, and therefore no external work is done. Since  $q = 0$  and  $w = 0$ , in the equation  $\Delta E = q - w$ , it follows that  $\Delta E = 0$ , i.e., the *internal energy of a given mass of a perfect gas is independent of the volume*. In mathematical terms for a perfect gas,

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \quad [18]$$

In fact this is one of the two important criteria for a perfect gas. (The other is conformance with Boyle's law.) Joule and Thomson have shown that this statement is only approximately true for actual gases. A change in temperature does occur when a real gas expands, owing to the fact that a certain amount of work is required to overcome the mutual attraction of the molecules for each other. This phenomenon is known as the Joule-Thomson effect.

In their investigation of the departure of real gases from ideal behavior, Joule and Thomson forced a continuous stream of gas, under a constant pressure higher than that of the atmosphere, through an insulated tube containing a porous plug of cotton or silk. They measured the temperature of the gas both before and after its passage through the plug, and found that air, oxygen, nitrogen, and carbon dioxide were all cooled by expansion whereas hydrogen gave a slight rise in temperature. The essential features of the experiment are represented diagrammatically in Fig. 38, in which  $P$  is the porous plug and  $A$  and  $B$  are two movable pistons. The work done in forcing a

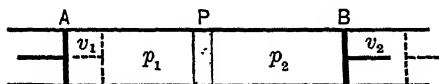


FIG. 38

mole of gas at volume  $v_1$  and pressure  $p_1$  through the plug is  $p_1 v_1$ . Similarly, on the opposite side of the plug, the work done by the gas in driving  $B$  outward against atmospheric pressure is  $p_2 v_2$ . Unless the gas is perfect, the work done in expansion at the outlet will not be equal to the work done in compression at the inlet. The external work performed by the system as a whole may be written

$$p_2 v_2 - p_1 v_1 = w$$

If the system is thermally insulated and the process is adiabatic,  $q = 0$ , and, according to equation (2),

$$\Delta E = E_2 - E_1 = -w = p_1 v_1 - p_2 v_2$$

or

$$E_2 + p_2 v_2 = E_1 + p_1 v_1$$

But

$$E_2 + p_2 v_2 = H_2, \quad \text{and} \quad E_1 + p_1 v_1 = H_1$$

hence

$$H_2 = H_1$$

It is apparent, therefore, that in the free expansion of a real gas, the heat content remains constant. In consequence of this fact, the Joule-Thomson coefficient,  $\mu$ , may be defined mathematically by the expression

$$\mu = \left( \frac{\partial T}{\partial p} \right)_H \quad [19]$$

For air at atmospheric pressure and  $0^\circ$ ,  $\mu$  has the value  $+0.4$ , indicating that a decrease in pressure of one atmosphere decreases the temperature  $0.4^\circ \text{C}$ . For hydrogen and helium at room temperature,  $\mu$  has negative values, or in other words these gases become warmer when forced through a porous plug. At temperatures below  $154^\circ \text{K}$ ., however,  $\mu$  becomes positive for hydrogen. It is evident that two factors are involved in the Joule-Thomson effect — an expansion against the force of attraction between the molecules (corresponding to  $a$  in van der Waals' equation), and a work term involving the change of  $p v$  with pressure. A more exact treatment is given in the appendix on page 663.

The Joule-Thomson coefficient,  $\mu$ , has been determined accurately over a wide range of temperatures and pressures by Roebuck\* and his co-workers for several gases. It is used not only in calculations for industrial processes such as the liquefaction of air but also for many thermodynamic quantities and the constants in equations of state for gases. One of the most accurate determinations of  $0^\circ \text{C}$ . on

\* Roebuck, Murrell, and Miller, *J. Am. Chem. Soc.*, **64**, 400 (1942); also earlier contributions.

the absolute temperature scale depends on the experimental evaluation of  $\mu$ .

**Adiabatic Expansion of a Gas.** In the adiabatic expansion of a gas the temperature falls, but there is no exchange of heat with the surroundings and  $dq = 0$ . Then by the first law

$$dE = dq - dw = -dw = -p dv$$

Referring to equations (17) and (18),  $dE = C_v dT$  for the adiabatic expansion of a perfect gas, and therefore

$$C_v dT = -p dV$$

Since for 1 mole of a perfect gas  $p = RT/V$  it follows that

$$C_v dT = -RT \frac{dV}{V}$$

and

$$C_v \frac{dT}{T} = -R \frac{dV}{V}$$

If  $V_1$  is the volume of the gas at the initial temperature  $T_1$  and  $V_2$  is the volume at the final temperature  $T_2$ , and if  $C_v$  is constant, integration between limits gives,

$$C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} \quad [20]$$

According to this equation when 1 mole of a perfect gas having a heat capacity  $C_v$  expands reversibly and adiabatically,  $V_2$  is greater than  $V_1$  and accordingly  $T_2$  must be less than  $T_1$ . In other words, the gas cools. It is evident also that adiabatic compression of the gas produces an increase in temperature. In solving problems it is necessary, of course, to express  $C_v$  and  $R$  in the same units.

*Example 4.* If a gas is compressed so rapidly that there is no opportunity to transfer heat to the container, the operation will be adiabatic. Calculate the temperature increase of a mole of helium which is compressed adiabatically from 44.8 liters at  $0^\circ$  to 22.4 liters. The molar heat capacity of helium is constant and equal to 3.00 cal. per degree.

$$C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

$$3.00 \times 2.303 \log \frac{T_2}{273.1} = -1.987 \times 2.303 \times \log \frac{22.4}{44.8}$$

$$\log T_2 = -\frac{1.987}{3.00} (\log \frac{1}{2}) + \log 273.1$$

$$T_2 = 432.4$$

$$\Delta T = 432.4 - 273.1 = 159.3^\circ$$

**Heat Capacity of Gases.** When a monatomic gas, such as helium or mercury vapor, is heated at constant volume, the heat energy supplied is used only to augment the translational kinetic energy of the molecules. Since there is no change in volume there can be no work done against the atmosphere, and, since there is only one atom in the molecule, there can be no absorption of vibrational or rotational energy within the molecule.

According to the fundamental kinetic equation given on page 34

$$pv = \frac{2}{3} \text{ kinetic energy} \quad [21]$$

or

$$\text{Kinetic energy} = \frac{3}{2}pv$$

But for 1 mole of a perfect gas

$$pV = RT = 1.987T$$

therefore

$$\text{Kinetic energy of 1 mole} = \frac{3}{2}RT = 3T \quad (\text{approximately}) \quad [22]$$

If  $3T_2$  represents the kinetic energy at temperature  $T_2$ , and  $3T_1$  at temperature  $T_1$ , the difference in kinetic energy is  $3(T_2 - T_1)$  calories. If now the difference in temperature is made exactly  $1^\circ$ , the difference in kinetic energy is 3 calories, and this value is the molar heat capacity at constant volume,  $C_v$ , defined as the number of calories necessary to raise 1 mole of the gas through  $1^\circ$ . For gases in which the energy can be absorbed only by increasing the translational velocity

$$C_v = 3 \text{ cal. per degree per mole} \quad [23]$$

It has been found that monatomic gases have a molar heat capacity  $C_v$  of 3 calories per degree in perfect agreement with this formula.

When a gas is heated at constant pressure the gas expands and does work against the atmosphere. Heat must be introduced into the gas to do this work as well as to raise the temperature. This work is equal to  $p \Delta V$ . If  $V_2$  is the volume at  $T_2$  and  $V_1$  is the volume at  $T_1$ , and  $T_2 - T_1 = 1^\circ$ , then for a perfect gas, in which the internal energy is independent of the volume,

$$\begin{aligned} C_p - C_v &= p \Delta V = p(V_2 - V_1) = R(T_2 - T_1) = R \\ &= 2 \text{ cal. mole}^{-1} \text{ degree}^{-1} \end{aligned} \quad [24]$$

Another proof of this equation is given in the appendix on page 662.

Since  $C_v = 3$  for monatomic gases, and  $C_p = C_v + 2$ , it follows that  $C_p = 5$ , and the ratio  $\gamma$  of the two heat capacities is

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.66 \quad [25]$$

Again, this relation is in excellent agreement with the experimental data for monatomic gases.

For polyatomic molecules the heat energy supplied is used not only in increasing the kinetic energy of translation in the three directions but also in increasing the energy of rotation and of vibration of the atoms within the molecule. If the extra energy absorbed is represented by  $g$ , then the ratio of the two specific heats will be

$$\gamma = \frac{C_p}{C_v} = \frac{5 + g}{3 + g} < 1.66 \quad [26]$$

The ratio becomes less than 1.66 in this case, and with increasing complexity of the molecule the value of  $g$  increases and the ratio  $\gamma$  becomes continuously smaller, but it cannot become less than 1.

There is nothing in equation (23) to indicate that the heat capacity of a monatomic gas is affected by temperature, but in equation (26) for polyatomic gases, it can be seen that, if  $g$  changes with temperature, both the heat capacities and their ratios may be influenced by a temperature change. As a matter of fact, the molar heat capacity of monatomic gases is found to be 3 cal. per degree at all temperatures but the heat capacity of polyatomic gases increases with increasing temperature. The extra energy  $g$  absorbed by polyatomic molecules becomes less as the temperature is lowered. At temperatures below 60° K., hydrogen,  $H_2$ , behaves as a monatomic gas and  $\gamma$  is found to have a value of 1.66.

In Table II the heat capacities of a few gases are given, and it will be seen that for monatomic gases  $C_v = 3$  and  $\gamma = 1.66$ ; that, for all gases,  $C_p$  is greater than  $C_v$  by about 2 cal. per degree; that  $C_p$  increases and  $\gamma$  decreases as the molecules become more complex. Most of the values given in this table refer to a temperature of 25° and pressure of 1 atm. In general an increase in temperature has no effect on the heat capacity of monatomic gases but it leads to a slight increase in the heat capacity of the polyatomic molecules, particularly the more complicated ones. Thus an increase of 100° causes  $C_p$  to increase by 0.01 in oxygen and 0.42 in carbon dioxide. Obviously, deductions based alone on an examination of a few gases in Table II cannot be considered general. However, they are supported by the theoretical deductions just given and by an extensive examination of many gases.

A table of constants for calculating the heat capacities of the common gases at different temperatures is given on page 122.

Attempts have been made to express the "complexity of the molecule" in more quantitative terms. A diatomic molecule (similar to a



TABLE II  
MOLAR HEAT CAPACITIES OF GASES  
(In cal. per mole at 25°)

Gas	$C_p$	$C_v$	$C_p/C_v = \gamma$
Argon, A	4.97	2.98	1.67
Helium, He	4.97	2.98	1.67
Mercury, Hg	4.97	2.98	1.67
Hydrogen, $H_2$	6.90	4.91	1.41
Oxygen, $O_2$	7.05	5.05	1.40
Nitrogen, $N_2$	6.94	4.95	1.40
Chlorine, $Cl_2$	8.25	6.14	1.34
Nitric oxide, NO	7.11	5.11	1.39
Carbon monoxide, CO	6.97	4.97	1.40
Hydrogen chloride, HCl	7.05	5.01	1.41
Carbon dioxide, $CO_2$	8.96	6.92	1.29
Nitrous oxide, $N_2O$	9.33	7.29	1.28
Sulfur dioxide, $SO_2$	9.4	7.3	1.29
Ammonia, $NH_3$	8.63	6.57	1.31
Methane, $CH_4$	8.60	6.59	1.31
Ethane, $C_2H_6$	12.71	10.65	1.19
Dimethyl ether, $C_2H_6O$	15.89	13.75	1.16

dumbbell) can absorb rotational energy by turning over on its axis, and it can absorb vibrational energy by oscillation of the atoms within the molecule. In complex molecules there can be rotations and different types of oscillation between different pairs or groups of atoms. These different ways of absorbing energy correspond to *degrees of freedom*. Theoretically each type of vibration or rotation might be expected to add either  $R$  or  $\frac{1}{2}R$  calorie per mole, respectively, to the heat capacity. It was shown in equation (22) that the translational energy in the three directions of space for a mole of gas is  $\frac{3}{2}RT$ . Thus, the energy in one direction, i.e., in one degree of freedom, is  $\frac{1}{2}RT$ . Some of these degrees of freedom tend to "freeze up" at low temperatures, and the extent to which they contribute to the heat capacity depends on rules which have been partly worked out by the quantum theory and which are discussed on page 554.

**Heat Capacity of Solids.** Studies of the specific heats of solids at extremely low temperatures have resulted in the formation of several interesting relationships between heat capacity and temperature. Einstein, Debye, and Nernst and Lindemann pioneered in this field.

At ordinary temperatures the molecules or atoms of a crystal may be assumed to be in a state of violent motion. As the temperature is lowered the number of possible oscillations steadily dimin-

ishes. Near the absolute zero, where the amplitude of the atomic oscillations is small, a crystalline solid may be assumed to possess the properties characteristic of a perfectly elastic body. In other words, the crystalline forces holding the units together would overshadow the feeble thermal forces tending to initiate atomic oscillations within the solid. Under these conditions the solid as a whole would exhibit the same behavior as a single molecule, that is to say, the solid would function as a perfectly elastic body.

On this assumption Debye has derived the following approximate equation, expressing the heat capacity of a solid,  $C_v$ , in terms of its absolute temperature,  $T$ ,

$$C_v = 465 \frac{T^3}{\theta^3} \quad [27]$$

In this equation  $\theta$  is a constant characteristic of each solid. The value of  $\theta$  varies between the limits  $\theta = 50$  for calcium and  $\theta = 1840$  for carbon. The agreement between the observed and calculated values of  $C_v$  has been found to be excellent up to  $T = \theta/12$ . In agreement with this equation it is found that the heat capacity of crystals approach zero at the absolute zero.

Debye's equation does not apply at higher temperatures since the solid is no longer behaving as one large molecule. The lighter the atoms and the greater the crystalline forces within the solid, the higher is the temperature required for the individual atoms to acquire appreciable independent kinetic energy.

At room temperatures most of the solid elements, except those of low atomic weight, have reached a temperature at which all the different ways of absorbing heat are utilized, and they have the limiting value of atomic heat capacity, as shown in Fig. 39. In 1819 Dulong and Petit discovered the interesting fact that *the product of the specific heat and the atomic weight of the solid elements is a constant, approximately 6.4*. This law of Dulong and Petit played an important part in the determination of atomic weights, for it served to show from a simple specific heat measurement what multiple of the combining weight should be taken for the atomic weight in order to obtain the constant 6.4.

Lewis has shown that the specific heat at constant volume is a more significant quantity than the specific heat at constant pressure. In the latter case there are secondary effects depending on the thermal expansion and compressibility which tend to mask the more fundamental relation. Lewis and Gibson\* found that the atomic heat capacity

\* Lewis and Gibson, *J. Am. Chem. Soc.*, **39**, 2554 (1917).

at constant volume and room temperature is 5.9 within 0.09 for all the elements heavier than potassium for which data were available.

It will be noted that this value of 5.9 for the atomic heat capacity of a crystal is nearly three times the gas constant. Moreover, it will be remembered that the heat capacity of a monatomic gas at constant volume is  $\frac{3}{2}R$ . There is a theoretical reason why the atomic heat capacity of a crystal should be twice that of a monatomic gas. In a monatomic gas heat is absorbed only in giving the molecule increased kinetic energy, but in a crystal the units of the lattice have definite positions and when they are displaced they acquire potential energy which is equal to the kinetic energy required to displace them. Twice as much heat energy then is necessary to raise the temperature  $1^\circ$ .

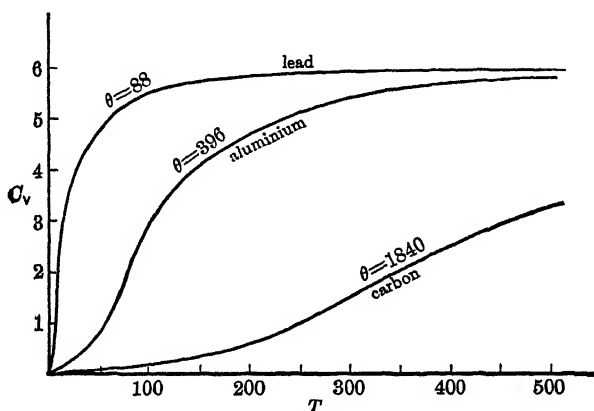


FIG. 39

The complete heat capacity curves for three typical solid elements, lead, aluminum, and carbon, are given in Fig. 39. It is apparent from these curves that the absorption of heat energy by a crystalline solid may be considered as taking place in three distinct stages, as follows: (1) in the neighborhood of the absolute zero, the heat capacity remains practically zero; (2) the heat capacity increases rapidly with the temperature; and (3) the heat capacity increases slowly, approaching asymptotically the limiting value 5.9 at high temperatures. For a malleable, low-melting element of high atomic weight, such as lead, the first two stages are very short and the final stage commences at a low temperature. With a hard, high-melting element of low atomic weight, such as carbon in the form of diamond, the final stage is not reached at any temperature within the range covered by the experiments.

These differences in behavior are now understood in terms of the

quantum theory (Chapter XIX) and for simple molecules can be calculated quantitatively from spectrographic data.

At very high temperatures the thermal agitation of the atoms may become so great as to impart some energy to the electrons, and, accordingly, under these conditions some elements like iron, which remain solid at high temperatures, possess atomic heat capacities greater than 5.9 cal. per degree.

In metals the electrons are only loosely held to the atoms. In fact, in some metals the electrons are not attached to any single atom. Accordingly the metals are excellent conductors of electricity.

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### PROBLEMS

1. A 900-g. weight falls 120 meters. (a) How many ergs of heat are liberated when it strikes the ground? (b) How many joules? (c) How many calories? (d) How many liter-atm?

*Ans.* (a)  $1.059 \times 10^{10}$  ergs. (b) 1059 joules. (c) 253.0 cal. (d) 10.45 liter-atm.

2. A piston whose diameter is 25 cm. moves 15 cm. under a pressure of 9 atm. How much work is done? *Ans.* 66.3 liter-atm.

3. A mole of a perfect gas is compressed isothermally and reversibly at 25° from 1 atm. to 9 atm. What is the value of  $w$  in calories? *Ans.* -1302 cal.

4. How many calories of heat is required to raise the temperature of 10 g. of argon (a monatomic gas) through 10° (a) at constant volume? (b) at constant pressure? *Ans.* (a) 7.5 cal. (b) 12.5 cal.

5. From the Dulong and Petit rule estimate the approximate specific heat of iron. *Ans.* 0.11.

6. What is the maximum work which can be obtained from the isothermal expansion of a gas at 27° from 10 atm. to 1 atm.?

7. One hundred grams of iron is dissolved in dilute acid at 25° giving a ferrous salt. Will more heat be evolved when the reaction is carried out in an open beaker or in a closed bomb? How much more?

8. Ten cubic feet of oxygen under pressure is allowed to expand reversibly under adiabatic conditions to a volume of 25 cu. ft. Considering oxygen to be a perfect gas with the average heat capacity given in the table, calculate the final temperature if the initial temperature is 25°.

9. Estimate the maximum rise in temperature of a 500-lb. iron weight when it hits a hard surface after falling through 1000 meters (neglecting air resistance). The atomic weight of iron is 55.85.

10. Estimate how many more calories of heat will be required to heat 100 g. of aluminum from 25 to 300° than will be required to heat the same weight of copper through the same temperature interval.

11. Calculate the heat capacity at constant pressure of 1000 g. of mercury vapor, which is monatomic.

12. The specific heat of neon at constant volume is 0.149. How many atoms are there in a molecule of neon?

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13. For the adiabatic expansion of a perfect gas show that

$$pV^\gamma = \text{constant}$$

and that

$$TV^{R/C_v} = \text{constant}$$

14. A perfect monatomic gas passes from a large pipe into an evacuated cylinder through a valve which is opened slowly enough to keep the pressure in the pipe sensibly constant. The gas in the main is at pressure  $P$  and temperature  $T$ . Develop a formula for calculating the temperature of the gas in the cylinder when its pressure reaches the pressure  $P$  of the pipe, if the gas loses no heat during the process.

15. For sulfur dioxide the values of van der Waals' constants are  $a = 6.714 \text{ l}^2 \times \text{atm.}$  and  $b = 0.05636 \text{ l.}$  Calculate the work done when a mole of  $\text{SO}_2$  at 27° expands reversibly and isothermally from 1 l to 10 l, assuming that the gas follows van der Waals' equation.

## CHAPTER VI

### THERMOCHEMISTRY

**Definitions.** Thermochemistry is concerned with the heat which accompanies chemical reaction.

Heat is a form of energy, and, as already shown, it may be resolved into two factors: an intensity factor, the temperature; and a capacity factor, the heat capacity.

The different units of heat energy are related as follows:

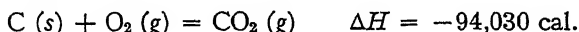
1 calorie (cal.) = 0.001 kilocalorie (kcal.) = 4.1833 international joules

Thermochemical data are usually expressed by writing the equation for the reaction and giving the value of  $\Delta H$  for the reaction. For example



It will be remembered that  $\Delta H$  is the heat of reaction at constant pressure. In equations it is the increase in heat content when 1 mole of the reactants, i.e., the chemical compounds written at the left of the equation, react to give the reaction products written at the right of the equation. The absolute values of the heat content are unknown and unnecessary. In the oxidation of carbon, heat is evolved and the heat content is thereby decreased, so that  $\Delta H$  has a negative value. As a matter of fact, most ordinary chemical reactions evolve heat. They are *exothermic* reactions and have negative values of  $\Delta H$ . At temperatures much higher than ordinary room temperatures the heat absorbing or *endothermic* reactions are more common.

In writing equations, solids, liquids, and gases are designated by (s), (l), and (g), respectively, and the preceding equation is written



If the units are not specified it may be assumed that  $\Delta H$  is expressed in calories.

Sometimes the symbols *l*, *s*, and *g* are omitted when there is no chance of confusion.

Another convention used in the thermochemistry of solutions is the symbol *aq.* (*aqua*, water) signifying a large excess of water, so large

that the addition of more water has no measurable effect on the temperature.

**Thermochemical Measurements.** Calorimeters are used for measuring the heat changes which accompany chemical reactions. In the most common type, the reaction is allowed to take place in a reaction chamber surrounded by a weighed quantity of water in an insulated vessel, and the rise in temperature is measured with a sensitive thermometer. The product of the rise in temperature and the total heat capacity of the water and calorimeter is a measure of the heat evolved. The heat capacity of the calorimeter is best obtained by measuring a reaction of known heat evolution, or by introducing a measured quantity of heat with an electrical heater. It is necessary to use reactions which proceed rapidly and definitely to completion, for otherwise the uncertainties in the cooling may introduce large errors. Heats of combustion in compressed oxygen are especially satisfactory in this respect. For this purpose combustion bombs of heavy steel are used. The same pressure of oxygen, 25 atm., is used for every measurement.

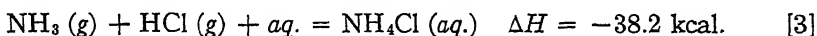
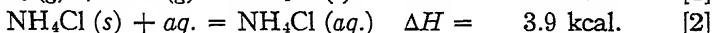
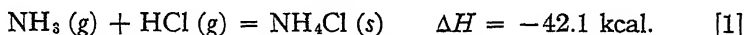
The water in the calorimeter must be stirred adequately to insure uniform temperature throughout. Absorption of heat due to evaporation of the liquid must be minimized, and the cooling of the heated calorimeter must be eliminated or corrected by calculation. Vacuum-walled vessels are used to minimize the heat losses, or the outer jacket is heated at a rate equal to the rate at which the calorimeter is heated. In this adiabatic method of calorimetry the calorimeter is always at the same temperature as its surroundings and no transfer of heat can take place. If these adiabatic methods are not followed it is necessary to apply a cooling correction. This correction is usually obtained by plotting the temperature at frequent time intervals and extrapolating the cooling curve of the final period back to the time at which the heating is started.

**Laws of Thermochemistry.** In 1780, Lavoisier and Laplace, as a result of their thermochemical investigations, stated that the quantity of heat which is required to decompose a chemical compound is equal to that which was evolved in the formation of the compound. This first law of thermochemistry will be seen to be a direct corollary of the law of the conservation of energy.

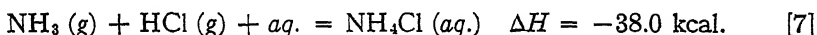
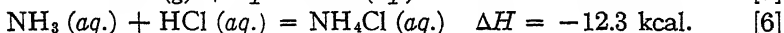
In 1840, Hess pointed out that the heat evolved in a chemical process at constant pressure is the same whether the process takes place in one or in several steps. This fact depends on the law of the conservation of energy. Since the total value of  $\Delta H$  depends only on the initial and final state, it is independent of the path. This is known as the law of constant heat summation. It may be illus-

trated by the equality of the heat of formation of ammonium chloride in aqueous solution, when prepared in two different ways. The results are the same within the limits of experimental error. The total amount of heat evolved in the formation and solution of ammonium chloride is the same, whether gaseous ammonia and hydrochloric acid are allowed to react and the resulting product is dissolved in water, or whether the gases are each dissolved separately and then allowed to react. Thus

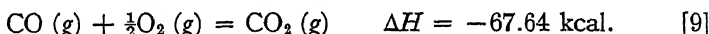
(A)



(B)



By means of the law of constant heat summation, it is possible to find indirectly the amount of heat evolved, or absorbed, by a reaction, even though it is impossible to carry it out experimentally. It is impossible, for example, to measure the heat evolved when carbon burns to carbon monoxide because burning carbon gives a mixture of carbon dioxide and carbon monoxide. But the heat evolved when carbon burns with an excess of oxygen to carbon dioxide can be accurately determined. Likewise the heat evolved in the combustion of carbon monoxide to give carbon dioxide may be readily measured. The equations are as follows:



Subtracting equation (9) from equation (8)



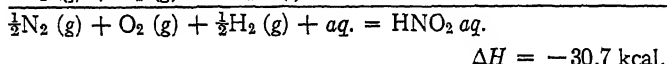
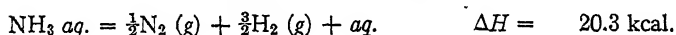
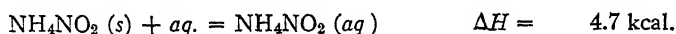
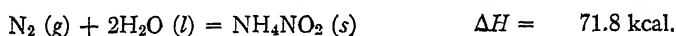
This indirect calculation of heats of reaction is illustrated with another example. The reactions for which the values of  $\Delta H$  are known are written down directly or in the reverse direction in such a way that the extra compounds not involved in the desired reaction will cancel out. When the reaction is reversed, the value of  $\Delta H$  will



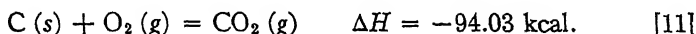
be reversed in sign. It may be necessary to try out several different equations, choosing from among the rapid reactions which have been accurately measured. When a suitable set of equations is found all the values of  $\Delta H$  are added together algebraically.

*Example 1.* What is the heat of reaction when aqueous nitrous acid is formed from its elements?

This reaction will not go directly, but it is known that solid ammonium nitrite decomposes into nitrogen and water with a measured evolution of heat. The latter reaction is used as a starting point and data for other reactions are sought which will indicate heat changes in passing from solid ammonium nitrite to aqueous nitrous acid. The problem is solved as follows:



**Heats of Formation.** Although the absolute heat contents of compounds may be unknown the *heats of formation* can be calculated by arbitrarily assuming that the heat content of the elements in their standard states is zero. For example, it follows from the reaction



that the heat of formation of carbon dioxide is  $-94,030$  cal., because  $94,030$  cal. of heat are evolved when a mole of carbon dioxide gas is produced from the elements, and the elements are arbitrarily assigned a zero value. The heat content of the elements will vary, depending on their physical state, and it is conventionally agreed that the standard states for which  $H$  is taken as zero are the naturally occurring states under 1 atm. pressure and at the temperature of the reaction. In the example given, oxygen is a gas at atmospheric pressure and carbon is a solid. Unless the temperature is specified it is assumed to be  $25^\circ \text{C}$ . If two or more allotropic forms can exist at the specified temperature, it is necessary to specify the form. Thus in this book graphite is always taken as the standard state for carbon and rhombic sulfur as the standard state for sulfur. Some authors have used diamond as the standard state for carbon.

The heats of formation of several inorganic and organic compounds are collected for reference in Table I.

TABLE I  
HEATS OF FORMATION AT 25°  
( $\Delta H$  in kcal. per mole)

*Inorganic Compounds*

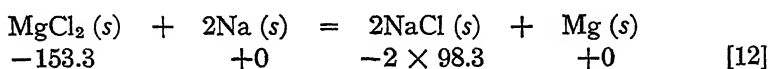
Na <sub>2</sub> O.....	-99.5	MgCl <sub>2</sub> .....	-153.3	PbSO <sub>4</sub> .....	-218.5
K <sub>2</sub> O.....	-86.2	PbCl <sub>2</sub> .....	-85.7	HCl (g).....	-22.1
CaO.....	-151.8	NaBr.....	-86.7	HBr (g).....	-8.7
FeO.....	-64.3	KBr.....	-94.1	HI (g).....	+5.9
Fe <sub>2</sub> O <sub>3</sub> .....	-198.5	AgBr.....	-23.8	H <sub>2</sub> O (l).....	-68.3
Fe <sub>3</sub> O <sub>4</sub> .....	-266.9	PbBr <sub>2</sub> .....	-66.3	H <sub>2</sub> O (g).....	-57.8
PbO.....	-52.5	NaI.....	-69.3	D <sub>2</sub> O (l).....	-70.4
Ag <sub>2</sub> O.....	-7.0	KI.....	-78.9	D <sub>2</sub> O (g).....	-59.6
HgO.....	-21.6	AgI.....	-14.9	NH <sub>3</sub> (g).....	-11.0
Na <sub>2</sub> S.....	-89.8	PbI <sub>2</sub> .....	-41.8	SO <sub>2</sub> (g).....	-70.9
K <sub>2</sub> S.....	-121.5	NaNO <sub>3</sub> .....	-111.7	H <sub>2</sub> SO <sub>4</sub> (l).....	-193.8
PbS.....	-22.3	KNO <sub>3</sub> .....	-118.1	N <sub>2</sub> O (g).....	+19.7
NaCl.....	-98.3	AgNO <sub>3</sub> .....	-29.4	NO (g).....	+21.6
KCl.....	-104.4	Pb(NO <sub>3</sub> ) <sub>2</sub> .....	-106.9	HNO <sub>3</sub> (l).....	-41.7
BaCl <sub>2</sub> .....	-205.3	Na <sub>2</sub> SO <sub>4</sub> .....	-330.5	C (diamond).....	+0.5
FeCl <sub>2</sub> .....	-81.9	K <sub>2</sub> SO <sub>4</sub> .....	-342.7	CO (g).....	-26.4
FeCl <sub>3</sub> .....	-96.4	BaSO <sub>4</sub> .....	-349.4	CO <sub>2</sub> (g).....	-94.0

*Organic Compounds*

Methane, CH <sub>4</sub> (g).....	-17.9	Cyclohexene, C <sub>6</sub> H <sub>10</sub> (l).....	-14.8
Ethane, C <sub>2</sub> H <sub>6</sub> (g).....	-20.2	Benzene, C <sub>6</sub> H <sub>6</sub> (l).....	+12.3
Propane, C <sub>3</sub> H <sub>8</sub> (g).....	-24.8	Thiophene, C <sub>4</sub> H <sub>4</sub> S (l).....	+19.6
n-Butane, C <sub>4</sub> H <sub>10</sub> (g).....	-29.7	Methanol, CH <sub>3</sub> OH (l).....	-57.0
iso-Butane, C <sub>4</sub> H <sub>10</sub> (g).....	-31.4	Ethanol, C <sub>2</sub> H <sub>5</sub> OH (l).....	-66.3
n-Pentane, C <sub>5</sub> H <sub>12</sub> (g).....	-34.8	n-Propanol, C <sub>3</sub> H <sub>7</sub> OH (l).....	-73.1
n-Pentane, C <sub>5</sub> H <sub>12</sub> (l).....	-41.1	n-Butanol, C <sub>4</sub> H <sub>9</sub> OH (l).....	-79.5
n-Hexane, C <sub>6</sub> H <sub>14</sub> (l).....	-47.6	Glycerol, C <sub>3</sub> H <sub>8</sub> O <sub>3</sub> (l).....	-158.6
n-Heptane, C <sub>7</sub> H <sub>16</sub> (l).....	-53.9	Formic acid, CH <sub>2</sub> O <sub>2</sub> (l).....	-99.5
n-Octane, C <sub>8</sub> H <sub>18</sub> (l).....	-60.3	Acetic acid, C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> (l).....	-116.7
Cyclohexane, C <sub>6</sub> H <sub>12</sub> (l).....	-37.7	Oxalic acid, C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> (s).....	-196.7
Ethylene, C <sub>2</sub> H <sub>4</sub> (g).....	+12.6	Succinic acid, C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> (s).....	-224.8
Propylene, C <sub>3</sub> H <sub>6</sub> (g).....	+4.8	Fumaric acid, C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> (s).....	-194.1
n-Butene-1, C <sub>4</sub> H <sub>8</sub> (g).....	+0.3	Maleic acid, C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> (s).....	-188.6
n-Pentene-1, C <sub>5</sub> H <sub>10</sub> (g).....	-5.0	Benzoic acid, C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> (s).....	-91.7

The calculation of heats of reaction is simplified by using the heats of formation when they are available. The change in heat content of a given reaction,  $\Delta H$ , is obtained by subtracting the heats

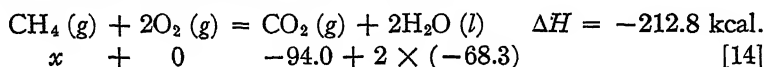
of formation of all the reacting materials from the heats of formation of all the products. The calculation is illustrated by the following reaction:



where the heats of formation are set under the compounds occurring in the equation. Then

$$\Delta H = (-2 \times 98.3 + 0) - (-153.3 + 0) = -43.3 \text{ kcal.} \quad [13]$$

In the same way heats of formation may be calculated from measured heats of reaction, as in the following example, where it is desired to find the heat of formation,  $x$ , of methane.

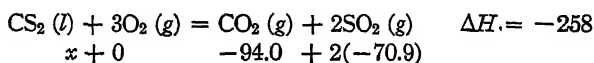


$$\Delta H = -212.8 = (-94.0 - 2 \times 68.3) - (x + 0) \quad [15]$$

$$x = -17.8 \text{ kcal.}$$

Another illustration is given for a compound which is formed from its elements with the absorption of heat, i.e., with a positive value of  $\Delta H$ . These endothermic compounds are less common and frequently they are unstable.

*Example 2.* Calculate the heat of formation of carbon disulfide from the elements carbon and sulfur at 25° if its heat of combustion at constant pressure is 258 kcal.



$$\Delta H = -258 = -94.0 - (2 \times 70.9) - (x + 0)$$

$$x = 22 \text{ kcal.}$$

**Reactions at Constant Pressure and Constant Volume.** As explained on page 94, when a reaction occurs at constant volume, no work is involved, but if the system is allowed to expand during the reaction it does work against the atmosphere and a smaller quantity of heat is evolved. If the system contracts, the heat evolved in a reaction at constant pressure is greater than that at constant volume by an amount equal to the work done on the system by the surroundings. If the products and the reactants have the same volume the heats of reaction at constant pressure are the same as those at constant volume.

The general equation relating  $\Delta H$  and  $\Delta E$  is given here:

$$\Delta H = \Delta E + p \Delta V = \Delta E + \Delta n RT \quad [16]$$

where  $\Delta H$  is the heat of reaction at constant pressure,  $\Delta E$  is the heat of reaction at constant volume, and  $p \Delta V$  is the work done by the system. Since liquids and solids occupy very small volumes, the term  $p \Delta v$  usually includes only the volumes of gases. The increase in the number of moles of gas is denoted by  $\Delta n$ , i.e., the number of moles of gaseous products minus the number of moles of gaseous reactants. The gases must be perfect for this equation to be exact.

Heats of reaction are usually given for conditions of constant pressure because most reactions are studied at constant pressure. Heats of combustion of liquids and solids, however, are usually measured at constant volume, and equation (16) is useful in converting one into the other.

*Example 3.*



What is the value of  $\Delta H$ , i.e., the heat of reaction at constant pressure?

$$\begin{aligned} \Delta H &= \Delta E + \Delta n RT = -780,500 - 1.5 \times 1.987 \times 298.1 \\ &= -780,500 - 889 = -781,389 \\ &= -7.814 \times 10^5 \text{ cal.} = -781.4 \text{ kcal.} \end{aligned}$$

The number  $-781,389$  should not be written as a final value because it implies that the result is known with an accuracy of one part in 781,389, whereas the experimental errors are so great that the value should not be expressed beyond four significant figures.

**Heat of Combustion.** The heat evolved in the complete oxidation of a substance is known as the *heat of combustion*. The values are given in terms of heat of combustion per gram, or better as heats of combustion per mole. Since only rapid, complete reactions are suitable for thermochemical measurement, heats of combustion have been by far the most common data of thermochemistry. A great deal of our present thermochemical knowledge goes back to the data of Thomsen and Berthelot of half a century ago. Richards and his co-workers made many measurements of much greater accuracy. For details of recent measurements and calculations the recent literature\* should be consulted.

It is essential to burn everything to its highest stage of oxidation

\* Rossini, *Bur. Standards J. Research*, **12**, 735 (1934);

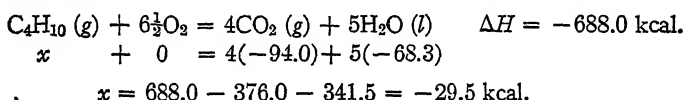
Richardson and Parks, *J. Am. Chem. Soc.*, **61**, 3543 (1939);

Huffman and Ellis, *J. Am. Chem. Soc.*, **57**, 41 (1935), and later papers.

to insure that a definite reaction is being measured which will give reproducible results. For this purpose the material is ignited electrically in a heavy steel bomb containing oxygen under a pressure of 25 atm. All carbon is burnt to carbon dioxide and all hydrogen to water. As yet the halogen-containing compounds present difficulties, and the heat of combustion of a substance like ethyl chloride is not known with high accuracy because the products formed are not always definite.

The molar heats of combustion are usually very large numbers so that a high order of accuracy is necessary for calculating heats of formation. These and other thermochemical data derived from them depend on differences between heats of combustion. Thus a fairly small percentage error in the heat of combustion may introduce a large error in the difference between two different substances.

*Example 4.* What per cent error in the calculation of the heat of formation of *n*-butane will be introduced by an error of 1 per cent in the heat of combustion of butane?



An error of 1 per cent in 688.0 is 6.88 kcal. An error of 6.88 in the heat of formation of butane is an error of 6.88/29.5 or 23.3 per cent.

If more accurate values for  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are used,  $-94.03$  and  $-68.32$  kcal., the value calculated for the heat of formation of *n*-butane is  $-29.7$  kcal. per mole, as in Table I.

The heats of combustion of a few substances are listed in Table II.

Heats of combustion are useful in calculating other thermochemical data, but also they have practical as well as theoretical importance. The heating value of fuel is an important matter. The purchaser of coal should be interested in its heat of combustion as well as in its weight. The dietician must know the calories obtainable from various foods as well as the vitamin and mineral content and other factors such as digestibility.

The heats of combustion of different allotropic forms of the elements are interesting. For example, when equal masses of diamond and graphite are burned successively in oxygen, the amounts of heat evolved are found to be quite different, as is shown by the following energy equations:

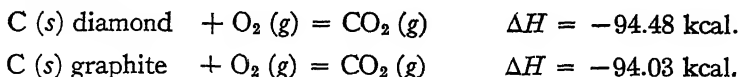
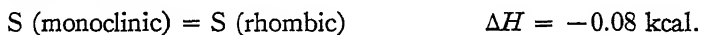


TABLE II  
HEATS OF COMBUSTION AT CONSTANT PRESSURE  
( $\Delta H$  in kcal. per mole at 25°)

Graphite, C.....	-94.0	<i>n</i> -Pentene-1, C <sub>5</sub> H <sub>10</sub> (g).....	-806.8
Diamond, C.....	-94.5	Cyclohexene, C <sub>6</sub> H <sub>10</sub> (l).....	-891.0
Methane, CH <sub>4</sub> (g).....	-212.8	Benzene, C <sub>6</sub> H <sub>6</sub> (l).....	-781.4
Ethane, C <sub>2</sub> H <sub>6</sub> (g).....	-372.8	Methanol, CH <sub>3</sub> OH (l).....	-173.7
Propane, C <sub>3</sub> H <sub>8</sub> (g).....	-530.6	Ethanol, C <sub>2</sub> H <sub>5</sub> OH (l).....	-326.7
<i>n</i> -Butane, C <sub>4</sub> H <sub>10</sub> (g).....	-688.0	<i>n</i> -Propanol, C <sub>3</sub> H <sub>7</sub> OH (l).....	-482.2
<i>iso</i> -Butane, C <sub>4</sub> H <sub>10</sub> (g).....	-686.3	<i>n</i> -Butanol, C <sub>4</sub> H <sub>9</sub> OH (l).....	-638.2
<i>n</i> -Pentane, C <sub>5</sub> H <sub>12</sub> (g).....	-845.3	Glycerol, C <sub>3</sub> H <sub>8</sub> O <sub>3</sub> (l).....	-396.8
<i>n</i> -Hexane, C <sub>6</sub> H <sub>14</sub> (l).....	-994.8	Formic acid, CH <sub>2</sub> O <sub>2</sub> (l).....	-62.8
<i>n</i> -Heptane, C <sub>7</sub> H <sub>16</sub> (l).....	-1150.8	Acetic acid, C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> (l).....	-208.0
<i>n</i> -Octane, C <sub>8</sub> H <sub>18</sub> (l).....	-1306.8	Oxalic acid, C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> (s).....	-59.7
Cyclohexane, C <sub>6</sub> H <sub>12</sub> (l).....	-936.4	Succinic acid, C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> (s).....	-356.2
Ethylene, C <sub>2</sub> H <sub>4</sub> (g).....	-337.3	Fumaric acid, C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> (s).....	-318.7
Propylene, C <sub>3</sub> H <sub>6</sub> (g).....	-491.8	Maleic acid, C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> (s).....	-324.1
<i>n</i> -Butene-1, C <sub>4</sub> H <sub>8</sub> (g).....	-649.7	Benzoic acid, C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> (s).....	-771.5

It is apparent that diamond has a greater heat content than graphite and, therefore, if this form of carbon were to undergo transformation into graphite, the reaction would be accompanied by the evolution of  $94.48 - 94.03 = 0.45$  kcal.

In like manner, the allotropic forms of both sulfur and phosphorus have different heats of combustion. The following equations express the differences in heat content between the allotropic forms of the two elements at 25°:



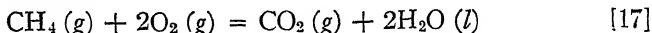
When the same substance is burned in oxygen, and then in ozone, it is found that more heat is evolved in ozone than in oxygen. The heat content equation expressing the change of ozone into oxygen may be written thus:



In simple reactions of this type it may not be necessary to determine the heat effect by obtaining differences in the very large heats of combustion. For example, the differences in heat of solution of rhombic and monoclinic sulfur in alcohol can be used for an accurate measure of the heat of transition.

Because the heats of combustion of organic compounds provide important information for making physical-chemical calculations,

attempts have been made to find empirical rules for estimating those heats of combustion of compounds which have not been determined with accuracy. For example, Thornton\* has shown that the molar heat of combustion at constant volume of any saturated hydrocarbon at room temperature is approximately  $-52.7$  kcal. for each atomic weight of oxygen required to burn it. To illustrate, the complete combustion of methane requires four atomic weights of oxygen as shown by the equation



The heat of combustion should then be

$$4 \times (-52.7) = -210.8 \text{ kcal.}$$

a value which is in good agreement with the  $-212.2$  kcal. found by direct measurement.

Kharasch† has developed a comprehensive method for estimating the heat of combustion of an organic substance from a knowledge of its molecular structure and the total number of electrons shifted in the formation of the  $\text{CO}_2$  molecules. The agreement with experimental measurements is very good. The original article must be consulted for details.

**Thermochemical Constants.** Thermochemical data are necessary for many calculations of theoretical significance in the predictions of chemical equilibria and reaction rates. It will be shown on page 536, for example, that when specific heat curves of reactants and products are known down to absolute zero, then a knowledge of the heat of reaction permits a simple and accurate calculation of the equilibrium constant of a chemical reaction. In many of these calculations the heats of reaction constitute the least satisfactory part of our available data.

In looking up thermochemical data one turns first to Bichowsky and Rossini's‡ critical compilation of heats of formation of inorganic compounds and the simpler organic compounds (less than four carbon atoms). If the material is not there it may be in International Critical Tables, Vol. V, p. 169,§ or possibly in the recent literature. Very accurate work on heats of combustion has been done by Rossini, by Parks, and by Huffman.||

\* Thornton, *Phil. Mag.*, **33**, 196 (1917).

† Kharasch, *Bur. Standards J. Research*, **2**, 359-430 (1929).

‡ Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, 1936.

§ "International Critical Tables," McGraw-Hill Book Co., New York, 1929.

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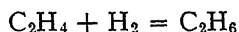
Heats of hydrogenation and bromination of unsaturated organic compounds have been determined accurately by Kistiakowsky\* and his co-workers.

If experimental data cannot be found directly or indirectly by combining several equations, one is forced to use approximation methods already mentioned. As a last resort one can estimate heats of reaction from the data of Table III by adding a definite number of calories for each bond broken in the reactants and subtracting a definite number for each bond formed in the products.

TABLE III  
HEATS OF DISSOCIATION OF BONDS

Bond	$\Delta H$ Dissociation, kcal.	Bond	$\Delta H$ Dissociation, kcal.
C—C	77	H—H	102
C=C	122	Br—Br	45
C≡C	200	N—H	96
C—H	92	=N—N=	33
C—Cl	79	N <sub>2</sub>	165
C—Br	58	O <sub>2</sub>	117
C—I	44	C—O	82
O—H	110	C=O	185

To illustrate the use of this table, the reaction



may be considered; one H—H bond and one C=C bond are broken, absorbing 224 kcal., whereas one C—C bond and two new C—H bonds are formed evolving 261 kcal. The net result is 37 kcal., which is in fair agreement with the correct value of 33 kcal.

This crude method leaves little allowance for structural features such as the formation of rings and conjugated double bonds, but progress is being made in explaining the extra heat involved in such structures by a consideration of the various possible arrangements of the electrons.

**Variation of Heat Capacity with Temperature.** In the preceding chapter (page 104), it was shown that the value of the molar heat capacity of a monatomic gas, at constant pressure, is 5.0 cal. per deg. According to the kinetic theory the molar heat capacity, at constant pressure, of all monatomic gases should be the same and independent

\* Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Am. Chem. Soc.*, **58**, 146 (1936), and other articles.



of the temperature. This theoretical requirement has been fully confirmed by experiments carried out at temperatures ranging from  $-80^{\circ}$  to  $200^{\circ}$ . The kinetic theory also indicates that the molar heat capacity of gases containing more than one atom per molecule should increase with the molecular complexity of the gas and with the temperature.

The changes in heat capacity with temperature for several simple gases are given in the empirical equations of Table IV.

TABLE IV  
MOLAR HEAT CAPACITIES OF GASES AT CONSTANT PRESSURE  
IN CAL. PER DEGREE  
 $(C_p = \Gamma_0 + \Gamma_1 T + \Gamma_2 T^2)$

Gas	$\Gamma_0$	$\Gamma_1 \times 10^3$	$\Gamma_2 \times 10^6$
H <sub>2</sub> <sup>3</sup>	6.62	0.81	....
N <sub>2</sub> <sup>3</sup>	6.76	0.606	0.13
O <sub>2</sub> <sup>3</sup>	6.76	0.606	0.13
CO <sup>3</sup>	6.60	1.2	....
HCl <sup>2</sup>	6.70	0.84	....
HBr <sup>2</sup>	6.80	0.84	....
HI <sup>2</sup>	6.93	0.83	....
Cl <sub>2</sub> <sup>2</sup>	8.28	0.56	....
F <sub>2</sub> <sup>3</sup>	6.50	1.00	....
S <sub>2</sub> <sup>2</sup>	7.75	0.89	....
H <sub>2</sub> O <sup>2</sup>	7.00	2.77	....
H <sub>2</sub> O <sup>3</sup>	8.22	0.15	1.34
CO <sub>2</sub> <sup>3</sup>	7.70	5.3	-0.83
H <sub>2</sub> S <sup>2</sup>	7.15	3.32	....
SO <sub>2</sub> <sup>3</sup>	7.70	5.30	-0.83
NH <sub>3</sub> <sup>1</sup>	6.70	6.30	....
CH <sub>4</sub> <sup>1</sup>	5.34	11.5	...

<sup>1</sup> From 300 to 800° K.

<sup>2</sup> From 300 to 1500° K.

<sup>3</sup> From 300 to 2500° K.

These heat capacity equations are important in many practical calculations, but data from which to determine them are very meager, particularly for the more complex molecules and the higher temperatures. Quite recently important progress has been made in deriving them from spectroscopic data with the aid of statistical mechanics (page 653). For the simple molecules the calculations are often more accurate than the calorimetrically determined data, especially at elevated temperatures.

To calculate the quantity of heat absorbed, it is necessary to inte-

grate the equation,  $dH = C_p dT$ , between the desired temperature limits.

*Example 5.* Calculate the amount of heat required to raise a mole of carbon dioxide from 25 to 200°.

$$\begin{aligned}\int_{298.1}^{473.1} dH &= \int_{298.1}^{473.1} (7.70 + 0.0053T - 0.00000083T^2) dT \\ \Delta H = H_{473.1} - H_{298.1} &= 7.70(473.1 - 298.1) + \frac{0.0053}{2} (473.1^2 - 298.1^2) \\ &\quad - \frac{0.00000083}{3} (473.1^3 - 298.1^3) \\ &= 1347.5 + 357.6 + 22.0 = 1727.1 \text{ cal.}\end{aligned}$$

It will be observed that all these equations are derived for constant pressure conditions, but they may readily be transformed so as to apply to constant volume conditions by subtracting 1.987 from the first term of each equation. On page 104 it was shown that the molar heat capacity of a gas is greater at constant pressure than at constant volume by  $R$ .

**Variation of Heat of Reaction with Temperature.** If a chemical reaction is allowed to take place at constant pressure first at temperature  $T_1$  and then at temperature  $T_2$ , the amounts of heat developed in the two cases may be quite different. Let us assume that the initial state of the system is represented by the point  $A$  in Fig. 40 and that the final state is represented by the point  $B$ . It is evident that we can pass from  $A$  to  $B$  by two independent paths at constant pressure, namely,  $AmB$  and  $AnB$ . According to the first law of thermodynamics the net absorption, or evolution, of heat must be the same by either path.

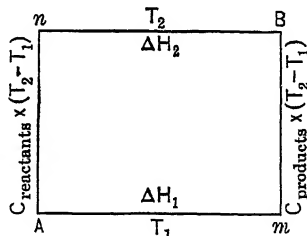


FIG. 40

Along the path  $AmB$  the reaction takes place at temperature  $T_1$  with the heat change  $\Delta H_1$  and the products are then heated from  $T_1$  to  $T_2$  along  $mB$ . The heat absorbed in this last stage is the heat capacity of the products multiplied by the temperature rise,  $C_{\text{products}}(T_2 - T_1)$ , assuming that  $T_2 - T_1$  is small.

Along the path  $AnB$  the reactants are first heated to temperature  $T_2$ , and the heat absorbed is the heat capacity of the reactants multiplied by the temperature rise,  $C_{\text{reactants}}(T_2 - T_1)$  over small tempera-

ture intervals. The reaction is then allowed to take place at temperature  $T_2$  with the heat change  $\Delta H_2$ . Then

$$\Delta H_1 + C_{\text{products}}(T_2 - T_1) = \Delta H_2 + C_{\text{reactants}}(T_2 - T_1) \quad [18]$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C_{\text{products}} - C_{\text{reactants}} = \Delta C_p \quad [19]$$

In this derivation it is assumed that the heat capacity does not change with temperature, but this assumption is not warranted over wide temperature ranges. The following equation is exact

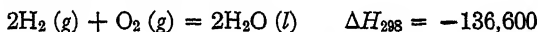
$$\frac{d(\Delta H)}{dT} = \Delta C_p \quad [20]$$

Integrating between  $T_1$  and  $T_2$

$$\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p dT \quad [21]$$

If a change of state from solid to liquid or vapor, for example, occurs while the temperature is being raised the heat absorbed in the change must be included; and if the heat capacity of the material is different after the change it is necessary to use a separate calculation.

*Example 6.* Calculate the heat of combustion of hydrogen at  $120^\circ$  from a knowledge of the heat of reaction at  $25^\circ$ .



Calculating  $\Delta H$  for the same reaction at  $100^\circ$ , using the molar heat capacities for  $\text{H}_2$  and  $\text{O}_2$  from Table IV, and assuming that the molar heat capacity of liquid water is 18 cal. throughout the whole temperature range,

$$\begin{aligned} \Delta H_{373} &= \Delta H_{298} + \int_{298}^{373} \Delta C_p dT = \Delta H_{298} + \\ &\quad \int_{298}^{373} [(2 \times 18) - 2 \times (6.62 + 0.81 \times 10^{-3}T) \\ &\quad - (6.76 + 0.606 \times 10^{-3}T + 0.13 \times 10^{-6}T^2)] dT = -136,600 + 36(373 - 298) \\ &\quad - [20.00(373 - 298) + \frac{1}{2}(0.002226)(373^2 - 298^2)] \\ &\quad - \frac{1}{3} \times 0.13 \times 10^{-6} \times (373^3 - 298^3) \\ &= -136,600 + 2700 - 1500 - 56 - 1 = -135,457 \end{aligned}$$

At temperatures just above  $100^\circ$  the product is steam instead of liquid water and sufficient heat is absorbed to vaporize the water, namely, 539.7 cal. per gram.

$$2\text{H}_2\text{O}(l) = 2\text{H}_2\text{O}(g) \quad \Delta H_{373} = 36.03 \times 539.7 = 19,445 \text{ cal.}$$

Then

$$\begin{aligned} 2\text{H}_2(g) + \text{O}_2(g) &= 2\text{H}_2\text{O}(g) \quad \Delta H_{373} = -135,457 + 19,445 \\ &= -116,012 \text{ cal.} \end{aligned}$$

Finally, for this reaction at 120°, giving steam, further calculation must be made using equation (22) and the molar heat capacities of steam, hydrogen, and oxygen.

$$\begin{aligned}\Delta H_{393} &= \Delta H_{373} + \int_{373}^{393} [2 \times (8.22 + 0.15 \times 10^{-3}T + 1.34 \times 10^{-6}T^2)] \\ &- [2 \times (6.62 + 0.81 \times 10^{-3}T) + (6.76 + 0.606 \times 10^{-3}T + 0.13 \times 10^{-6}T^2)] dT \\ &= -116,091 \text{ cal.}\end{aligned}$$

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## PROBLEMS

1. The heat of solution of  $\text{BaCl}_2$  is  $-2070$  cal. and the heat of hydration to  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  is  $-6970$  cal. What is the heat of solution of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ?

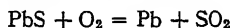
*Ans.*  $\Delta H = 4900$  cal.

2. In an adiabatic calorimeter, the combustion of 1.6324 g. of sucrose produces a temperature rise of  $2.854^\circ$ . The molar heat of combustion of sucrose is  $1349.6$  kcal.

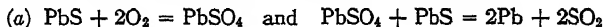
(a) What is the total heat capacity of the water and the calorimeter?

(b) If the calorimeter contains 1850 g. of water (specific heat = 1.0), what is the effective heat capacity of the calorimeter? In this problem, corrections for the oxidation of the wire and residual nitrogen may be neglected. *Ans.* 405.

3. Compute the heat evolved, per mole of lead, in the smelting of lead



from the data on the heats of formation and the equations



Check the calculation using the equations



*Ans.*  $\Delta H = -48.6$  kcal.

4. Calculate the heat of formation of liquid ethanol from the fact that the heat of combustion is  $\Delta H = -326.7$  kcal., and the heats of formation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are  $-94.0$  and  $-68.3$  respectively. *Ans.*  $-66.2$ .

5. Calculate the heat of combustion of liquid cyclohexane  $\text{C}_6\text{H}_{12}$  at  $20^\circ$  at constant volume. When this liquid is oxidized to carbon dioxide and water at constant pressure,  $\Delta H = -937.8$  kcal. *Ans.*  $\Delta E = -936.1$  kcal.

6. For the compound
- $\text{CHClF}_2$

$$C_v = 10.44 + 0.0230t$$

where

$$C_v = \text{calories per (mole)}(^{\circ}\text{C.})$$

$$t = ^{\circ}\text{C.}$$

This relationship holds from 35 to 135°. Calculate the change in internal energy  $\Delta E$  of the gas in going from 35 to 135°. *Ans.* 1239 cal. per mole.

- 7.
- $\text{H}_2\text{O}(g) + \text{C} \rightarrow \text{CO} + \text{H}_2$
- $\Delta H = 31,404$
- cal. at 25°.

$$C_p(\text{H}_2\text{O}) = 7.187 + 0.002373T$$

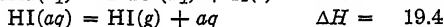
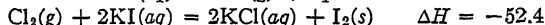
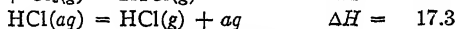
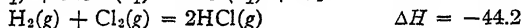
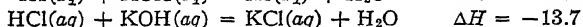
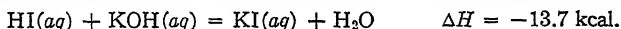
$$C_p(\text{C}) = 2.673 + 0.002617T - \frac{1.169 \times 10^5}{T^2}$$

$$C_p(\text{CO}) = 6.60 + 0.00120T$$

$$C_p(\text{H}_2) = 6.62 + 0.00081T$$

Calculate  $\Delta H$  at 400° C.*Ans.* 32,340 cal.

8. Calculate the heat of formation of hydriodic acid from the following data:



9. In an adiabatic calorimeter, 0.4362 g. of naphthalene caused a rise of 1.707° in temperature. The heat capacity of the calorimeter and water was 2460 cal. per degree. Neglecting corrections for the wire and residual nitrogen, what is the heat of combustion of naphthalene per mole?

10. Calculate the heat evolved in the thermite reaction at 25°  $2\text{Al} + \text{Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$ . When aluminum is oxidized to  $\text{Al}_2\text{O}_3$ ,  $\Delta H = -380,000$  cal. Show that if the reactants and products are both at 25° it makes no difference in the isothermal heat of reaction if the system is heated to a high temperature and then cooled again.

11. Calculate the heat of complete combustion of 1 mole of *n*-butane gas in a bomb calorimeter at 25°.

12. The equation for the molar heat capacity of
- n*
- butane is:

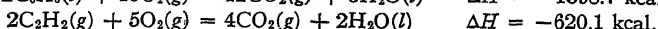
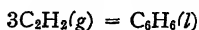
$$C_p = 4.64 + 0.0558T$$

Calculate the amount of heat necessary to raise the temperature from 25 to 200°.

13. Using the necessary data in the tables, calculate the heat evolved in the reaction  $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$  at 823°.

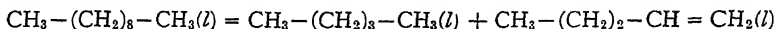
14. Estimate the molar heat of combustion of *n*-nonane,  $\text{C}_9\text{H}_{20}$ , from the data on octane, heptane, and hexane.

15. (a) From some of the following thermochemical equations at 17° and at constant pressure, calculate the heat evolved at constant pressure in the reaction



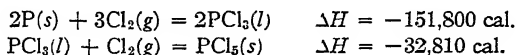
(b) Calculate the heat evolved when the reaction is carried out at constant volume.

16. From the heat of combustion data given, calculate  $\Delta H_{293}$  for the following reaction:



<i>Compound</i>	<i>Heat of Combustion</i>
$\text{CH}_3-(\text{CH}_2)_8-\text{CH}_3(l)$	1610.2 kcal./mole
$\text{CH}_3-(\text{CH}_2)_3-\text{CH}_2(l)$	833.4 kcal./mole
$\text{CH}_3-(\text{CH}_2)_2-\text{CH} = \text{CH}_2(l)$	803.4 kcal./mole

17. (a) Calculate the heat of formation of  $\text{PCl}_5(s)$ , given the heats of the following reactions at  $25^\circ$ :



(b) State precisely what data would be needed to calculate the heat of formation of  $\text{PCl}_5(s)$  at some other temperature.

18. Calculate the heat of combustion of liquid cyclohexane at  $25^\circ$  at constant volume. When cyclohexane,  $\text{C}_6\text{H}_{12}$ , is oxidized at constant pressure  $\Delta H = -936.4$  kcal. at  $25^\circ$ .

19. For methane  $C_p = 5.34 + 0.0115T$ . With this fact and data from this chapter, calculate  $\Delta H_{1000}$  for the reaction  $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$ .

20. One thousand grams of ice at its melting point is added to 1000 g. of water at  $100^\circ$  contained in an iron dish weighing 200 g. What will be the final temperature, neglecting heat losses to the surroundings?

21. Estimate the heats of the reactions (a)  $\text{C}_2\text{H}_6 + 2\text{Br}_2 = \text{C}_2\text{H}_4\text{Br}_2 + 2\text{HBr}$ ; (b)  $\text{C}_2\text{H}_4 + \text{Br}_2 = \text{C}_2\text{H}_4\text{Br}_2$ .

22. One B.T.U. or British Thermal Unit is the heat required to raise the temperature of a pound of water  $1^\circ \text{F}$ . (B.T.U. per pound equals calories per gram.)

(a) Calculate the heat evolved by the complete combustion at constant pressure and  $25^\circ$  of 1 cu. ft. of water gas ( $\frac{1}{2}\text{CO}$  and  $\frac{1}{2}\text{H}_2$  by volume) measured at  $25^\circ$  and 1 atm.

23. The heat of formation of  $\text{C}_2\text{H}_5\text{Br}$  is  $-19.3$  kcal. Estimate the strength of the H—Br bond, using data of Tables I and III

24. As a rough approximation, the molar heat capacity of a *solid* is of the same order of magnitude as the sum of the atomic heat capacities of the solid elements of which the solid compound is formed. What general statement can be made regarding the influence of temperature on the heat of reactions of solids to give solids, as for example, the reaction  $\text{Fe} + \text{S} = \text{FeS}$ ?

25. For the following reaction  $\Delta H = 47.16$  kcal.:



Calculate the heat of formation of ketene,  $\text{CH}_2\text{CO}(g)$ , obtaining additional data from tables of thermochemical data.

## CHAPTER VII

### THERMODYNAMICS

**The Second Law of Thermodynamics.** Although work can always be transformed into heat, it does not follow that heat can be transformed completely into work. The first law of thermodynamics given on page 91 merely specifies that, when heat is converted into work, a definite quantitative relationship exists between the heat converted and the work done, but it tells nothing as to the maximum amount of work which can be obtained from a given quantity of heat. The second law of thermodynamics gives information as to the limitations which experience has shown govern the transformation of heat into work. It states that heat cannot pass from a colder to a hotter body unless work is supplied from an outside source. In general heat can pass spontaneously only from a higher temperature to a lower temperature just as a body of water can flow only from a higher level to a lower level. Again, an engine operating in a cycle can do work only when there is a transfer of heat from a higher to a lower temperature.

A kinetic explanation is helpful. If one end of a tube of gas is hot and the other end cold, heat will flow from the hot end to the cold and in so doing could do work. But after the motions of molecules have become averaged throughout, and the whole tube is at a uniform temperature, it is extremely improbable that the more rapidly moving molecules would all move spontaneously to one end causing the tube to become hot at one end and cold at the other. In fact, it is far less likely than that a pack of cards after being shuffled should by continued shuffling return to the original order. It is less likely because the number of molecules is much greater than the number of cards in a pack and the laws of probability hold better when large numbers are involved.

The second law of thermodynamics may be applied to a variety of phenomena. It may be stated in a more general way as follows: *All systems tend to approach a state of equilibrium.* The movement of molecules of a dissolved substance from a region of high concentration to a region of low concentration giving uniform concentration throughout the whole solution is merely another manifestation of the second

law. The running down of a clock or the reaction of zinc and sulfuric acid are other illustrations.

The second law is statistical, and like all statistical laws it breaks down when only a small number of individuals is involved. For example, if there are more small particles moving around on one side of a microscopic field than on the other side the general tendency is for particles to migrate from the region of high concentration to the region of low concentration until the concentration is uniform throughout, but occasionally it will be observed that a particle moves in the opposite direction making the low concentration still lower, contrary to the prediction. When there is a large number of particles this occasional movement against the general traffic becomes comparatively rarer.

**Entropy.** In order to express the second law in concise mathematical form it is useful to introduce the concept of entropy. The change in entropy of a system ( $dS$ ) for an infinitesimal, *reversible* process is defined by the equation

$$dS = \frac{dq_{\text{rev.}}}{T} \quad [1]$$

where  $dq_{\text{rev.}}$  is the heat absorbed from the surroundings. For any *natural* process complete reversibility can never be attained on account of such effects as frictional losses which accompany practical operations, and

$$dS > \frac{dq}{T} \quad [2]$$

In these equations  $T$  is the absolute thermodynamic temperature; if (in the case of an irreversible change) the temperature is not uniform, the highest temperature in the system and its surroundings should be used. These two equations, together with the statement that *the entropy change of a system depends only on the initial and final states of the system*, constitute the second law of thermodynamics. They may be shown to be equivalent to the other forms of this law given above.

It is important to realize that entropy is a property which is independent of the previous history of the system, as are pressure, internal energy, and index of refraction, for example. Hence when a substance changes from one given state to some other definite state, no matter by what reversible or irreversible process, the entropy change is the same. It is merely the difference in the values of this property in the two states. For example, let us consider several processes



by which a mole of perfect gas initially at 25° and 10 atm. pressure is expanded to a final pressure of 1 atm. and final temperature 25°. If the gas is expanded reversibly and isothermally from 10 atm. to 1 atm., the entropy change will be the same as when it is expanded into an evacuated vessel of such size that the final pressure will be 1 atm. Another process might consist in heating the gas at constant pressure to 100°, expanding it isothermally to 1 atm., and then cooling it at constant pressure to 25°. In each case the entropy of the gas increases by the same amount, but only when the process is reversible can equation (1) be used to evaluate the change.

A feeling for the meaning of entropy may be obtained by consideration of an isolated system. Since heat cannot be removed or added, in this case  $dq = 0$  and we have for spontaneous or natural changes

$$dS > 0 \quad [3]$$

That is to say, the entropy tends to increase. For reversible processes, i.e., equilibrium processes, in an isolated system, by equation (1)

$$dS = 0 \quad [4]$$

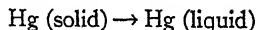
and so entropy remains constant after equilibrium is reached. Hence the possibility of change in the entropy is a measure of how far an isolated system is from equilibrium. Alternatively, the entropy may be interpreted as a function of the probability of the thermodynamic state; the tendency for the entropy of an isolated system to increase corresponds to the tendency of the system, if left alone, to go to a state of higher probability. It is also a measure of the disorder of a system. The more the molecules in a system are distributed in a random manner the more probable is the arrangement and the greater is the entropy. The most orderly arrangement would be a crystal at absolute zero, and according to the third law of thermodynamics, which will be discussed in Chapter XVIII, the entropy of a crystal at absolute zero is zero.

**Entropy Calculations.** A few concrete examples of entropy calculations will now be offered. The transfer of heat from one body to another at constant temperature is a reversible process if the direction of heat flow may be reversed by infinitesimal changes in the temperature of one of the bodies. The fusion of a solid at its melting point or the evaporation of a liquid at a constant pressure equal to its vapor pressure are examples of isothermal, reversible processes in which the entropy change is readily visualized and easily calculated.

Integration of equation (1) yields, when  $T$  is constant,

$$S_2 - S_1 = \Delta S = \frac{q_{\text{rev.}}}{T} \quad [5]$$

*Example 1.* Solid mercury melts at  $-38.9^\circ \text{C.}$  with the absorption of 560 cal. per mole. The process is isothermal, and the melting may be easily reversed by lowering the temperature of the surroundings infinitesimally; so the process must be reversible.



$$\Delta S = \frac{q_{\text{rev.}}}{T} = \frac{560}{234.2} = 2.39 \text{ cal. per degree} = 2.39 \text{ entropy units}$$

The molal entropy of a liquid is always greater than that of the solid at the freezing point.

Entropy has the dimensions of energy divided by absolute temperature, and the usual entropy units, e.u., are given in calories per degree. Heat capacity also has the dimensions of calories per degree, but the two are of course not the same.

The entropy increase involved in raising the temperature of a substance may be calculated also. The heat absorbed is equal to the heat capacity  $C$  multiplied by the increase in temperature, and if the changes are kept infinitesimally small the process is reversible. Thus

$$dq_{\text{rev.}} = C dT$$

and

$$dS = \frac{dq_{\text{rev.}}}{T} = \frac{C dT}{T} \quad [6]$$

As the temperature is raised each infinitesimal absorption of heat must be divided by the temperature at which the absorption takes place, a calculation which is readily made with the help of calculus. Integrating between the limits  $T_1$  and  $T_2$

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} C dT/T \quad [7]$$

If  $C$  is constant

$$S_2 - S_1 = C (\ln T_2 - \ln T_1) = C \ln \frac{T_2}{T_1} = 2.303C \log \frac{T_2}{T_1} \quad [8]$$

This formula is equally applicable for constant pressure or constant volume. If the heating is carried out at constant pressure  $C_p$  is used, and if it involves constant volume  $C_v$  is used. Chemical oper-

ations usually involve constant pressure. The integration of (6) can also be carried out if the heat capacity is not constant but is known as a function of temperature, such as is given on page 122.

*Example 2.* Calculate the increase in entropy involved in heating a mole of liquid mercury at constant pressure from 234.2 to 298.1° K. The average molal heat capacity at constant pressure over this temperature is 6.70 cal. per degree.

$$\Delta S = S_2 - S_1 = 2.303 \times 6.70 \log 298.1/234.2 = 1.71 \text{ cal. per degree.}$$

*Example 3.* When a mole of supercooled water freezes isothermally at  $-10^\circ \text{C.}$  what is the change in entropy? The process is irreversible. In order to calculate the entropy change the process must be carried out in steps, every one of which is reversible, and the absorption or evolution of heat is measured in each reversible step. Thus

$$\text{H}_2\text{O (liquid) at } -10^\circ \rightarrow \text{H}_2\text{O (liquid) at } 0^\circ. \quad \Delta S = \int_{-10^\circ}^{0^\circ} C_{\text{liq.}} \frac{dT}{T}$$

$$\text{H}_2\text{O (liquid) at } 0^\circ \rightarrow \text{H}_2\text{O (solid) at } 0^\circ. \quad \Delta S = \frac{q_{\text{rev.}}}{T}$$

$$\text{H}_2\text{O (solid) at } 0^\circ \rightarrow \text{H}_2\text{O (solid) at } -10^\circ. \quad \Delta S = \int_{0^\circ}^{-10^\circ} C_{\text{ice}} \frac{dT}{T}$$

The crystallization of liquid water at  $0^\circ \text{C.}$  evolves  $80 \times 18 \text{ cal.}$  The specific heat of water is 1.0 cal. per degree and that of ice is 0.5 cal. per degree over this range. Then  $\Delta S = \left(18 \times 1.0 \times 2.303 \log \frac{273}{263}\right) + (18 \times (-80)/273) + \left(18 \times 0.5 \times 2.303 \log \frac{263}{273}\right) = 0.67 - 5.28 - 0.34 = -4.95 \text{ cal. per degree.}$  The entropy is greater in the liquid form. ( $\Delta S$  for the surroundings is not considered here.)

**Free Energy and Work Content.** Two other thermodynamic functions, work content and free energy, have been invented for convenience in studying processes at constant temperature. The work content and free energy of a phase are defined by the equations

$$A = E - TS \quad [9]$$

$$F^* = H - TS \quad [10]$$

Like entropy and the other quantities in terms of which they are defined,  $F$  and  $A$  depend only on the state of the system. They are extensive properties. Of these concepts free energy is perhaps the most useful in its application to chemical problems because it pro-

\* This function, called free energy and given the symbol  $F$  by G. N. Lewis, was given the symbol  $\zeta$  by Willard Gibbs.

vides a convenient quantitative measure of the extent to which substances can unite chemically. It permits the calculation of chemical equilibria as explained later on page 289. The practical importance of equation (10) in such calculations will be discussed on page 539.

Using the definition of  $H$ ,

$$H = E + pv \quad [11]$$

we see at once that

$$F = E + pv - TS \quad [12]$$

and also, from equation (9)

$$F = A + pv \quad [13]$$

The absolute values of  $A$  and  $F$ , like those of  $E$  and  $H$ , are not known. We are concerned, however, only with the changes in these quantities, and in passing from the initial to the final state we may write, for example,

$$A_2 - A_1 = E_2 - E_1 - (T_2 S_2 - T_1 S_1)$$

or

$$\Delta A = \Delta E - \Delta(TS) \quad [14]$$

$$\Delta F = \Delta H - \Delta(TS) \quad [15]$$

$$\Delta F = \Delta A + \Delta(pv) \quad [16]$$

These equations are more useful under certain specific restrictions; thus at constant temperature

$$A_2 - A_1 = E_2 - E_1 - (TS_2 - TS_1)$$

or

$$\Delta A = \Delta E - T \Delta S \quad [17]$$

at constant temperature

$$\Delta F = \Delta H - T \Delta S \quad [18]$$

at constant pressure

$$\Delta F = \Delta A + p \Delta v \quad [19]$$

Of these last six equations which follow at once from the definitions of  $A$ ,  $F$ , and  $H$ , equation (18) and (19) are most frequently used in physical chemistry.

For changes at constant temperature  $\Delta A$  has a physical meaning easy to grasp. In this case equation (17) applies, and if we consider a process which is reversible as well as isothermal,

$$T \Delta S = q.$$

But by the first law

$$\Delta E - q = -w$$

and so

$$\Delta A = -w \quad [20]$$

If the identical change is brought about by some other process,  $\Delta A$  will be the same, and if this other process is reversible and isothermal, equation (20) shows that the work also will be the same. On the other hand, the work done on the surroundings when a process is carried out irreversibly is less than if it is carried out reversibly. Hence we conclude that at constant temperature

$$-\Delta A = w_{\max}. \quad [21]$$

In words, the decrease in work content, as its name implies, equals the maximum amount of work which can be obtained isothermally.

The significance of  $\Delta F$  at constant temperature and pressure, where it is most useful, can easily be seen from equations (21) and (19). Combining

$$-\Delta F = w_{\max}. - p \Delta v \quad [22]$$

Since  $p \Delta v$  is here the expansion work, this means that if the temperature and pressure are kept constant the decrease in free energy equals the maximum available work other than expansion work, i.e., other than the work involved in increasing the volume of the system against a resisting pressure.

For any infinitesimal change we see by differentiation of equation (13)

$$dF = dA + p dv + v dp \quad [23]$$

If the process is reversible and isothermal, and the work restricted to that due to volume changes, from equation (21)

$$dA = -dw_{\max} = -p dv \quad [24]$$

Adding (23) and (24)

$$dF = v dp \quad [25]$$

and

$$\left( \frac{dF}{dp} \right)_T = v$$

At constant temperature, therefore, the rate of change of free energy with pressure equals the volume. If the system is a perfect gas,

integration of (25), the temperature remaining constant, yields,

$$\int dF = \int \frac{n RT}{p} dp$$

$$F = n RT \ln p + \text{constant} \quad [26]$$

or integrating between limits,  $F_1$  and  $p_1$  being the initial values and  $F_2$  and  $p_2$  being the final values,

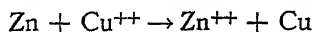
$$\Delta F = F_2 - F_1 = n RT \ln \frac{p_2}{p_1} \quad [27]$$

This equation should now be compared with equation 6 on page 97, remembering that  $pv = n RT$ . Or, if the system is a liquid or a solid which may be considered incompressible, we have upon integrating (25)

$$\Delta F = F_2 - F_1 = v(p_2 - p_1) \quad [28]$$

Since the free energy depends only on the state of the system, these equations hold even if the change is brought about by an irreversible process, but the restriction to constant temperature and to work of the expansion type must be remembered.

**Application to a Chemical Reaction.** The chemical significance of heat content, free energy, and entropy may be illustrated with the reaction by which copper is precipitated from a solution of copper sulfate by the addition of zinc under conditions of constant temperature and constant atmospheric pressure. The reaction is

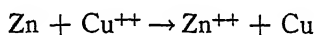


The change in *heat content* may be obtained by simply measuring the heat evolved when zinc is added to an open calorimeter containing the copper sulfate. The rise in temperature multiplied by the heat capacity of the solution and calorimeter gives directly  $-q_p$  or  $-\Delta H$ .

The change in *free energy* may be obtained by carrying out the reaction in an electrical cell made by dipping a zinc rod into a solution of zinc sulfate and a copper rod into a solution of copper sulfate and connecting the two solutions with a tube of solution or a porous plate. This little battery will operate a motor and do work which can be measured, but the maximum work obtainable is determined more accurately with a potentiometer and galvanometer (as described on page 428) under conditions such that the voltage is measured when very little current is flowing. Zinc is consumed and copper deposited by the operation of the cell, but by increasing the applied voltage

slightly above the voltage of the cell, the cell may be operated backwards so that copper is consumed and zinc deposited. In other words the process can be reversed by infinitesimal changes, and hence this is a way in which the reaction can be carried out reversibly. Then by equation (22) the electrical work measured under these conditions equals the change in free energy ( $-\Delta F$ ). The expansion work  $p \Delta v$ , due to the change in volume of the solution when the reaction occurs, is not measured by the potentiometer. The change in work content ( $-\Delta A$ ) for the reaction, according to equation (21) is equal to the electrical work plus the  $p \Delta v$  work.

The change in entropy ( $\Delta S$ ) when zinc is added to a solution of copper sulfate in a calorimeter cannot be determined by dividing the heat of reaction by the absolute temperature because the reaction carried out in this way is not reversible. Only reversible processes can be used in the calculation of entropy by equation (5). It is necessary to measure the heat evolved or absorbed when the reaction is carried out reversibly. For example, the zinc-copper battery just described can be placed in a calorimeter and the heat which is evolved or absorbed can be measured while the cell is operating reversibly. This quantity of heat for the reversible process, divided by the absolute temperature, gives the entropy change which accompanies the reaction



no matter how it is carried out, for  $\Delta S$  depends only on the initial and final states.

If a considerable current is drawn from the battery so that the process is not reversible, the work will be less than the maximum, and the heat absorbed will be less than for the reversible case. This latter statement follows from equation (2), which upon integration becomes

$$\Delta S > \frac{q}{T} \quad [29]$$

for an irreversible, isothermal process.

**Spontaneous Changes.** The second law affords criteria for equilibrium and for deciding whether or not a process can possibly take place of itself. Thus by equation (2) if  $T dS > dq$ , the process is a natural one, that is, it is possible for it to take place spontaneously. If  $T dS = dq$ , the process is reversible or in other words the system is at equilibrium with respect to changes of the particular type. In the case of a system *isolated from its surroundings*, so that no heat

can be absorbed, the conditions are somewhat simpler:  $\Delta S > 0$  for spontaneous changes and  $\Delta S = 0$  for changes taking place at equilibrium; changes for which  $\Delta S < 0$  are not possible without outside help.\*

For a system which is not isolated but rather kept at constant temperature and pressure the free energy provides a more convenient criterion for equilibrium and for natural changes. These are the conditions under which many chemical processes are carried out and hence free energy is very important in physical chemistry. We may start with the equation

$$F = E + pv - TS \quad [30]$$

At constant temperature and pressure,

$$\Delta F = \Delta E + p \Delta v - T \Delta S \quad [31]$$

From equations (1) and (2)

$$q \leq T \Delta S \quad [32]$$

with the equality holding for reversible processes and the inequality holding for spontaneous processes at constant temperature. By the first law of thermodynamics

$$\Delta E = q - w \quad [33]$$

and hence on adding equation (31), (32), and (33) we obtain

$$\Delta F \leq -w + p \Delta v. \quad [34]$$

For systems subjected to no external forces other than pressure, equation (34) simplifies to

$$\Delta F \leq 0 \quad [35]$$

because under these conditions the only work done is the pressure-volume work. Therefore, if in a process involving only expansion work at constant temperature and pressure there is a decrease in free energy, the change is a natural one; if there is no change in free energy the system is at equilibrium with respect to that process; and if the free energy increases, the process is impossible *under these conditions*.

Water and ice have the same free energy per mole at 0° C. and 1 atm. pressure, and the two are in equilibrium. There is no tend-

\* It may be recalled that in Example 3 the *isothermal* freezing of supercooled water at -10° is accompanied by a decrease in entropy. But in this case the system is not isolated. If the supercooled water were isolated thermally in a vacuum bottle, it would not change completely into ice.



ency for ice to melt or water to freeze in a mixture at  $0^{\circ}\text{C.}$  and 1 atm. On the other hand, the free energy of water supercooled to  $-10^{\circ}\text{C.}$  is higher per mole than that of ice at the same temperature and pressure of 1 atm. The change of water to ice at this temperature and pressure is accompanied by a decrease in free energy and hence is a natural change. The change in the reverse direction, since for it  $\Delta F > 0$ , cannot take place spontaneously.

In a similar manner it may be shown that at constant temperature and volume, if no work of any kind is done, the criterion for a spontaneous process is

$$\Delta A < 0 \quad [36]$$

and for an equilibrium process

$$\Delta A = 0 \quad [37]$$

These relations are summarized in Table I.

TABLE I  
CRITERIA FOR EQUILIBRIUM AND SPONTANEOUS PROCESSES

	Spontaneous	Equilibrium	Not Spontaneous
$\Delta S$ ( $q = 0$ )	+	0	—
$\Delta F$ ( $T$ and $p$ constant)	—	0	+
$\Delta A$ ( $T$ and $v$ constant)	—	0	+

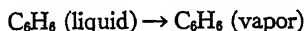
By saying that these criteria may show that a certain process is a natural or spontaneous one does not mean that the process necessarily will take place with an appreciable speed. Thus a mixture of one mole of carbon and one mole of oxygen at one atmosphere pressure and  $25^{\circ}$  has a free energy greater than that of 1 mole of carbon dioxide at 1 atm. and  $25^{\circ}$ , and so it is possible for the carbon and oxygen to combine to form carbon dioxide at this constant temperature and pressure. However, thermodynamics has nothing to say about the time that will be required, and carbon may exist for a very long time in contact with oxygen; but the reaction is possible and will take place slowly. The reverse process — the decomposition of carbon dioxide — involves an increase in free energy, and it can occur only with the aid of an outside agency or by heating to a very high temperature where the free energy change has the opposite sign.

Early attempts to discover a relation between thermodynamics and the direction of spontaneous chemical reactions led Berthelot in 1879 to the false conclusion that the evolution of heat in a chemical reaction is a measure of chemical affinity. The mere existence of spontaneous reactions which absorb heat and the general reversibility of all reactions under suitable conditions show that this conclusion cannot be right. In some cases, however, where the entropy change is very small, it serves as a rough approximation. This statement follows from the relation  $\Delta F = \Delta H - T \Delta S$  at constant temperature and the criterion  $\Delta F < 0$  for spontaneous processes under the conditions usual for carrying out chemical reactions. If  $T \Delta S$  is small compared with  $\Delta F$ , as is often true, then  $\Delta H$  and  $\Delta F$  will have the same sign and approximately the same magnitude;  $\Delta H$  will then be negative and heat will be evolved in the spontaneous reaction.

A qualitative principle known as the theorem of Le Chatelier has been useful in predicting the direction in which a change may be expected. According to this theorem, if a system at equilibrium is disturbed, the system will shift in such a way as to minimize the effect of the disturbance. For example, if pressure is applied to ice, the ice melts to give liquid water, which has a smaller volume, and the pressure is relieved. Other examples will be given in later chapters.

**Thermodynamic Calculations.** The various thermodynamic quantities  $q$ ,  $w$ ,  $H$ ,  $F$ ,  $S$ ,  $E$ , and  $A$ , will be understood best through the quantitative relations which connect them. In this section simple physical processes will be considered. Applications to chemical processes will be found throughout the book. In considering the application of thermodynamic formulas to a given problem the various restrictions under which these formulas were derived must be borne in mind and it is well to consider: (a) What are the initial and final states? (b) Is the process reversible or not? (c) Is it isothermal or not? (d) Is it isobaric or not, i.e., is it carried out at constant pressure?

*Example 4.* One mole of benzene is vaporized at the boiling point  $80.2^\circ$  or  $353.3^\circ$  K. under a pressure of 1 atm. The heat of vaporization measured in a calorimeter at constant pressure is 94.4 cal. per gram. Calculate  $w$  and  $q$  and each of the thermodynamic quantities  $\Delta H$ ,  $\Delta E$ ,  $\Delta A$ ,  $\Delta F$ , and  $\Delta S$ . The process is



and it is carried out reversibly, isothermally, and at a constant pressure of 1 atm.

$$q_p = \Delta H = 94.4 \times 78.11 = 7374 \text{ cal. per mole}$$

Assuming that the volume of the liquid is negligible in comparison with that

of the vapor and that the vapor obeys the simple gas laws,

$$w = p \Delta V = p(V_{\text{vapor}} - V_{\text{liquid}}) \cong^* p V_{\text{vapor}} = RT$$

$$= 1.987 \times 353.3 = 702 \text{ cal. per mole}$$

$$\Delta E = \Delta H - p \Delta v = 7374 - 702 = 6672$$

$$\Delta A = -w_{\text{max}} = -p \Delta v = -702$$

Also 
$$\Delta F = \int v dp = 0$$

or 
$$\Delta F = \Delta A + p \Delta v = -702 + 702 = 0$$

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{7374}{353.3} = 20.87 \text{ e.u.}$$

Also 
$$\Delta S = \frac{\Delta H - \Delta F}{T} = \frac{7374 - 0}{353.3} = 20.87 \text{ e.u.}$$

*Example 5.* One mole of a perfect gas at  $27.0^\circ$  changes its pressure from 10 atm. to 1 atm. by expanding isothermally and reversibly against a pressure which is gradually reduced. Calculate each of the thermodynamic quantities. Calculations with the simple gas equation show that the volume expands from 2.462 liters to 24.62 liters  $\left(24.62 = \frac{0.08205 \times 300.1}{1}\right)$ .

The process is carried out isothermally and reversibly but the pressure is not constant.

$$w_{\text{max}} = RT \ln \frac{V_2}{V_1} = 1.987 \times 300.1 \times 2.303 \log \frac{24.62}{2.462}$$

$$= 1.987 \times 300.1 \times 2.303 \times 1 = 1373 \text{ cal.}$$

$$\Delta A = -w_{\text{max}} = -1373 \text{ cal.}$$

$$\Delta E = 0$$

since the internal energy of a perfect gas is not affected by a change in volume.

$$q = \Delta E + w = 0 + 1373 = 1373 \text{ cal.}$$

$$\Delta H = \Delta E + \Delta(pv) = 0 + 0 = 0$$

since  $p v$  is constant for a perfect gas at constant temperature.

$$\Delta F = \int_{10}^1 v dp = RT \left[ \ln p \right]_{10}^1 = 1.987 \times 300.1 \times 2.303(-1) = -1373 \text{ cal.}$$

Also,

$$\Delta F = \Delta A + \Delta(pv) = -1373 + 0 = -1373 \text{ cal.}$$

$$\Delta S = \frac{q_{\text{rev.}}}{T} = \frac{1373}{300.1} = 4.58 \text{ e.u.}$$

\* The symbol  $\cong$  is used to indicate an approximate equality.

Also,

$$\Delta S = \frac{\Delta H - \Delta F}{T} = \frac{0 - (-1373)}{300.1} = 4.58 \text{ e.u.}$$

*Example 6.* One mole of a perfect gas expands isothermally at  $27^\circ$  into an *evacuated* vessel until the pressure drops from 10 atm. to 1 atm.; i.e., it expands from a vessel of 2.462 liters into a connecting vessel such that the total volume is 24.62 liters. Calculate the change in thermodynamic quantities.

This process is isothermal but it is *not* reversible and the pressure is not constant.

$w = 0$  because the system as a whole is closed and no external work can be done.

$q = 0$  because according to the Joule-Gay Lussac effect there is no heat change in the vessel as a whole during the expansion of a perfect gas.

$\Delta A$  and  $\Delta F$  cannot be calculated directly from  $w$  because the work is not maximum work, and  $\Delta S$  is not equal to  $q/T$  because the heat is not measured in a reversible process. But these quantities are independent of the path, and their differences between initial and final state are identical with those of the preceding example (5) carried out under conditions which permit their calculation.

Then,

$$\Delta F = -1373 \text{ cal.}, \Delta A = -1373 \text{ cal.}, \Delta H = 0, \Delta E = 0, \Delta S = 4.58 \text{ e.u.}$$

**Conversion of Heat into Work.** When a system goes through a series of changes which bring it back to its original state (a cyclic process) no work can be produced from heat absorbed if the temperature is maintained constant. However, when a condenser is available at a lower temperature, heat can be converted into work, and the maximum work obtainable can be calculated as shown in the following derivation. A reversible engine is assumed, for only in a reversible process can the maximum work be obtained.

Consider an engine which performs the following steps reversibly (Carnot cycle):  $q_2$  units of heat are taken in at temperature  $T_2$ , the temperature is changed to  $T_1$  by an adiabatic process (such as adiabatic expansion of a gas in the engine),  $q_1$  units of heat are rejected to the condenser at the lower temperature  $T_1$ , and finally the cycle is completed by an adiabatic process which raises the temperature to  $T_2$  and restores the system to its original state. The engine gains entropy  $q_2/T_2$  at the higher temperature, loses entropy  $q_1/T_1$  at the lower temperature, and suffers no change in entropy in the adiabatic steps, because in these steps  $q = 0$ . The entropy change in the engine is zero for a complete cycle because the engine returns to its original condition and therefore to its original entropy. Entropy

depends only on the state of the system irrespective of its previous history. Then

$$\frac{q_2}{T_2} - \frac{q_1}{T_1} = 0 \quad [38]$$

For the complete cycle  $\Delta E$  is zero also, and by the first law the work done per cycle is given by

$$w = q_2 - q_1 \quad [39]$$

Solving (38) for  $q_1$  and substituting in (39) we obtain

$$w_{\max} = q_2 \frac{T_2 - T_1}{T_2} \quad [40]$$

wherein we have explicitly indicated that the work obtained is a maximum, since the process is reversible.

This important equation, which may be regarded as a mathematical statement of the second law of thermodynamics, is independent of the properties of the substance in the engine and of the engine itself, provided it undergoes a Carnot cycle. It shows that the maximum fraction of heat which can be converted into work in a Carnot cycle, i.e.,  $w_{\max}/q_2$  or the maximum efficiency of the process, is equal to the difference in temperature divided by the higher absolute temperature. If the condenser could be placed at absolute zero all the heat would be available for doing work, and the maximum efficiency would be unity. This equation (40) finds important applications in engineering.

*Example 7.* What is the maximum work that can be obtained from 1000 calories of heat supplied to a water boiler at  $100^\circ$  if the condenser is at  $20^\circ$ ?

$$w_{\max} = q_2 \frac{T_2 - T_1}{T_2} = (1000) \frac{373.1 - 293.1}{373.1} = 214 \text{ cal.}$$

If the boiler temperature is raised to  $150^\circ$  by the use of superheated steam under pressure, how much more work can be obtained?

$$w_{\max} = (1000) \frac{423.1 - 293.1}{423.1} = 307 \text{ cal.}$$

$$307 - 214 = 93 \text{ cal. more}$$

Mercury engines have been successfully operated, and their thermodynamic efficiency is higher than that of steam engines because the boiler temperature is  $723^\circ \text{K.}$ ; but the advantage is offset by the initial cost of mercury, the great weight, and the danger from poisoning.

A relation of the same form as (40) was derived by Carnot for a perfect gas put through a Carnot cycle, which in this case consists of an isothermal expansion at  $T_1$ , adiabatic expansion to  $T_2$ , isothermal compression at  $T_2$ , and finally an adiabatic compression to  $T_1$ . The details are given in the appendix on page 664. The second law as derived in equation (40) is perfectly general whereas the Carnot cycle is derived only for a perfect gas.

The temperature used in deriving equation (40) was introduced in equations (1) and (2) and called the thermodynamic absolute temperature without further discussion, whereas the temperature used in the derivation in the appendix leading to the same relation is the absolute temperature of ordinary usage, defined in terms of the properties of perfect gases. Hence, both temperature scales are essentially the same, and if one degree on the thermodynamic scale is taken equal to  $1^\circ \text{C.}$ , the scales become identical.

**The Gibbs-Helmholtz Equation.** Another important relation is obtained by differentiating equation (10) with respect to temperature at constant pressure.

$$\left(\frac{\partial F}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p - T \left(\frac{\partial S}{\partial T}\right)_p - S \quad [41]$$

The second and third terms are both equal to  $C_p$ . They cancel out, leaving

$$\left(\frac{\partial F}{\partial T}\right)_p = -S \quad [42]$$

In words, the derivative of free energy with respect to temperature at constant pressure is equal to the negative of the entropy.

Substituting the equivalent of  $-S$  from equation (10)

$$\left(\frac{\partial F}{\partial T}\right)_p = \frac{F - H}{T} \quad [43]$$

or taking the values of  $F$  and  $H$  in the initial and final states of an isothermal process

$$\left(\frac{\partial \Delta F}{\partial T}\right)_p = \frac{\Delta F - \Delta H}{T} \quad [44]$$

According to this equation, the difference between the change in free energy and the change in heat content for an isothermal process, divided by the absolute temperature, is equal to the rate at which the difference in free energy changes with temperature, when the pressure is kept constant.

This important equation is known as the Gibbs-Helmholtz equation. It will be illustrated in detail in a later chapter (page 431).

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### PROBLEMS

1. A mole of steam is condensed at  $100^{\circ}$  and the water is cooled to  $0^{\circ}$  and frozen to ice. What is the entropy change? Consider that the average specific heat of liquid water is 1.0. Heats of vaporization and fusion are 539.7 and 79.7 per gram.  
*Ans.*  $\Delta S = -36.9$ .

2. One mole of mercury is vaporized at its boiling point  $357^{\circ}$  under reversible conditions. The heat of vaporization is 65 cal. per g. Calculate: (a)  $q$ , (b)  $w$ , (c)  $\Delta H$ , (d)  $\Delta E$ , (e)  $\Delta F$ , (f)  $\Delta A$ , (g)  $\Delta S$ .

*Ans.* (a) 13,040 cal. (b) 1252 cal.  
 (c) 13,040 cal. (d) 11,788 cal.  
 (e) 0. (f) -1252 cal.  
 (g) 20.7 cal. per degree.

3. One mole of nitrogen is heated from 0 to  $110^{\circ}$  under a pressure of 2 atm. Calculate (a) the increase in heat content; (b) the increase in internal energy, assuming nitrogen to be a perfect gas. The average specific heat of nitrogen at constant pressure is 0.244.  
*Ans.* (a) 752 cal. (b) 534 cal.

4. One liter of a perfect gas at  $300^{\circ}$  K has an initial pressure of 15 atm. and is allowed to expand isothermally to a volume of 10 liters.

- (a) Calculate the maximum work which can be obtained from the expansion.  
 (b) What is  $\Delta E$ ?  
 (c) What is  $\Delta H$ ?  
 (d) Calculate  $\Delta F$ .  
 (e) Calculate  $\Delta A$ .

*Ans.* (a) 34.5 liter-atm. (b) 0. (c) 0. (d) -34.5 liter-atm.  
 (e) -34.5 liter-atm.

5. One gram of gasoline evolves 11,200 cal. of heat on combustion.

(a) If used to run a steam engine with the boiler at  $105^{\circ}$  and the condenser at  $30^{\circ}$  what is the maximum work in calories which can be obtained?

(b) If used in an explosion engine with the temperature in the cylinder at  $2200^{\circ}$  and the exit temperature at  $1200^{\circ}$  what is the maximum work obtainable?

*Ans.* (a) 2222 cal. (b) 4529 cal.

6. A thermostat is maintained at a temperature of  $96.9^\circ$ . The air in the room is at  $26.9^\circ$ . During a certain length of time 1000 cal. of heat leaked through the thermostat insulation into the room.

(a) What was the entropy change of the material in the thermostat?

(b) What was the entropy change of the air in the room?

(c) Was the process reversible or irreversible?

Ans. (a)  $-2.70$  e.u. (b)  $3.33$  e.u. (c) Total entropy change =  $0.63$  e.u., therefore irreversible.

7. Calculate the entropy change involved in heating 100 g. of helium from  $0$  to  $1000^\circ$  at constant pressure.

8. Tabulate: (a)  $w$ , (b)  $q$ , (c)  $\Delta H$ , (d)  $\Delta E$ , (e)  $\Delta F$ , (f)  $\Delta A$ , (g)  $\Delta S$  when 1 mole of steam is compressed reversibly to liquid water at the boiling point  $100^\circ$ . The heat of vaporization of water at  $100^\circ$  and 760 mm. is 539.7 cal. per g.

9. Ten grams of helium is compressed isothermally and reversibly at  $126.9^\circ$  from a pressure of 5 atm. to 10 atm. Calculate (a)  $q$ , (b)  $w$ , (c)  $\Delta F$ , (d)  $\Delta A$ , (e)  $\Delta H$ , (f)  $\Delta E$ , (g)  $\Delta S$ .

10. Calculate each of the quantities listed in Problem 9 for the isothermal compression of the helium not reversibly, but with a pressure of 10 atm. applied directly.

11. Compare the thermodynamic efficiency of a steam engine with that of a mercury vapor engine if the boiler of the former operates at  $100^\circ$  and the boiler of the latter operates at  $360^\circ$ , the condenser in each case operating at  $30^\circ$ .

12. Theoretically, how high could a gallon of gasoline lift an automobile weighing 3200 lb. against the force of gravity, assuming that the cylinder temperature is  $2200^\circ$  and the exit temperature  $1200^\circ$ ? (Density of gasoline = 0.8; 1 lb. = 453.6 g.; 1 liter = 0.2642 gal. Heat of combustion of gasoline = 11,200 cal. per g.)

13. Five moles of  $\text{NH}_3$  (considered to be a perfect gas) initially at  $25^\circ$  and 1 atm. pressure is heated at constant pressure until the volume has trebled. Calculate (a)  $q$ , (b)  $w$ , (c)  $\Delta H$ , (d)  $\Delta E$ , (e)  $\Delta S$ . For  $\text{NH}_3$ ,  $C_p = 6.70 + 0.0063T$ .

14. Calculate the differences between the atomic entropies of  $\text{Hg}(l)$  and  $\text{Hg}(s)$  at  $-50^\circ$ . The melting point of Hg is  $-39^\circ$  and the heat of fusion is 560 cal. per gram-atom. The heat capacity per gram-atom of  $\text{Hg}(l)$  may be taken as  $7.1 - 0.0016T$  and that of  $\text{Hg}(s)$  as 6.4 cal. per degree.

15. (a) Calculate the external work done against the atmosphere when 1 mole of toluene is vaporized at its boiling point,  $111^\circ$ . The heat of vaporization at this temperature is 86.5 cal. per g.

For the vaporization of 1 mole calculate (b)  $q$ , (c)  $\Delta H$ , (d)  $\Delta E$ , (e)  $\Delta F$ , (f)  $\Delta A$ , (g)  $\Delta S$ .

16. Calculate the free energy change undergone by 1 mole of water, when (a) it is evaporated at its boiling point, and (b) it is expanded in its vapor state from 30.5 to 50 liters at  $100^\circ$ .

17. In the reversible isothermal expansion of a perfect gas at  $200^\circ \text{K}$  from 1 liter to 10 liters, where the gas has an initial pressure of 20 atm., calculate (a)  $\Delta S$  for the gas, (b)  $\Delta S$  for all systems involved in the expansion, (c)  $\Delta A$  for the gas, (d)  $\Delta A$  for all systems involved in the expansion.

18. Discuss the advantages and disadvantages of using diphenyl instead of water for an engine. Diphenyl boils at  $254.6^\circ$  and melts at  $70.5^\circ$ .

19. How much work must be done in a refrigerating machine, operating in a Carnot cycle between 0 and  $25^\circ$ , in order to freeze 50 kg. of water?



20. For a reversible process the net  $\Delta S$  for all systems involved is equal to zero. Show that in an *isothermal* process the net  $\Delta A$  for all systems involved is also equal to zero.

21. One mole of a perfect diatomic gas ( $C_v = 5$ ) initially at  $40^\circ$  and 10 atm. pressure expands quickly (adiabatically) against a constant external pressure of 2 atm. until its own pressure has fallen to 2 atm. Calculate  $\Delta S$  for the operation.

22. An isothermal irreversible process takes place at  $300^\circ$  K. so that the net gain in entropy for all systems involved is  $+10.0$  entropy units. Calculate the minimum amount of work which would have to be transformed into heat at  $300^\circ$  K. to restore the systems involved to their previous state.

23. A 2-liter container at  $0^\circ$  contains  $H_2S$  (assumed to be an ideal gas) at 1 atm. pressure. The gas is heated to  $100^\circ$ , the external pressure remaining 1 atm. Calculate (a) the heat absorbed, (b) the work done, (c)  $\Delta E$ , (d)  $\Delta H$ , and (e)  $\Delta S$ . For  $H_2S$ ,  $C_p = 7.15 + 0.00332T$ .

24. One-half mole of an ideal monatomic gas initially at  $25^\circ$  and occupying a volume of 2 liters is allowed to expand adiabatically against a constant pressure of 1 atm. until external and internal pressures are equal. The gas is then compressed isothermally and reversibly until its volume is 2 liters at the lower temperature. Calculate (a)  $q$ , net heat absorbed, (b)  $w$ , net work done, (c)  $\Delta E$ , (d)  $\Delta H$ , and (e)  $\Delta S$ .

25. A system at a temperature of  $300^\circ$  K., under a constant pressure of 1 atm. and occupying a volume of 2 liters, is heated to a temperature of  $400^\circ$  K. During the heating, the system absorbs 10 cal. per degree rise in temperature. The system occupies a volume of 3 liters at  $400^\circ$  K. Calculate (a)  $\Delta E$ , (b)  $\Delta H$ , (c)  $\Delta S$ .

26. (a) Calculate the least work which would have to be performed in order to extract 100 cal. of heat from an ice bath at  $0^\circ$ , when the surroundings are at  $25^\circ$ .

(b) How much heat at  $25^\circ$  could be obtained from the ice bath upon the expenditure of 10 cal. of work?

27. In any reversible process, the net change in entropy for all systems involved is zero. Show that the  $\Delta F$  for all systems involved is zero in an *isothermal* reversible process for which the sum of the changes in the  $pv$  products for all systems involved is zero.

## CHAPTER VIII

### LIQUIDS

**General Characteristics of Liquids.** A liquid has no definite shape but it does retain a definite volume under given conditions. The distance between molecules is much less in liquids than in gases as illustrated by the fact that a mole of water at its normal boiling point occupies 18.8 ml. but when vaporized it occupies about 30,200 ml. at 1 atm. pressure. This closer proximity of the molecules in the liquid state results in a lesser fluidity and smaller effects from temperature and pressure changes.

The internal energy in the vapor state is greater than in the liquid state because it is necessary to supply energy in order to overcome the force of attraction which holds the molecules close together in the liquid.

A liquid may be regarded as a condensed gas or as a melted solid, and each point of view is important. The theory of the liquid state is in a much less satisfactory state than the theories of gases and crystals, but important progress is being made in our understanding of the structure of liquids.\*

At any instant liquids do possess something analogous to a definite arrangement between neighboring molecules as shown by the patterns they exhibit when x rays are passed through them. Moreover they require the expenditure of energy when one layer of liquid is forced past another. These facts and many more seem to be best explained on the hypothesis that the molecules are squeezed together by their own forces of mutual attraction but that each molecule has a free volume surrounding it, in which it behaves effectively as a perfect gas. In a solid the molecules cannot move from one place to another but in a liquid they can, provided that a small amount of energy is supplied. The thermodynamic properties of a liquid, such as vapor pressure, specific heat, and entropy of fusion, can be expressed in terms of this free volume.

**Liquefaction of Gases.** More than a century ago, Faraday liquefied practically all the gases which condense at moderate pressures and not too low temperatures. He inverted a sealed-off U-tube, and heated

\* Hirschfelder, "The Structure of Liquids," *J. Chem. Educ.*, **16**, 540 (1939).

one end while the other was immersed in a freezing mixture. Thus, when crystals of chlorine hydrate were heated in this tube the liberated chlorine gas was put under such a high pressure that it condensed to a yellow liquid in the cold end of the tube.

In 1834 Thilorier liquefied carbon dioxide in rather large amounts and observed that the evaporating liquid became sufficiently cold to freeze. He was able to obtain a temperature of  $-100^{\circ}\text{C}$ . by placing a mixture of solid carbon dioxide and ether under reduced pressure.

The following principles are involved in the liquefaction of gases: (1) the gas must be below its critical temperature; (2) the pressure must be great enough to cause liquefaction, and the lower the temperature the lower is the required pressure; (3) the incoming gas is cooled by the outgoing gas which has been cooled by expansion; (4) the gas is cooled by doing external work in an engine; and (5) it is cooled by expanding against the force of attraction between the molecules as explained in the discussion of the Joule-Thompson effect on page 101.

Air was first liquefied in large quantities in 1895. The operating principle of the Linde process and the Claude process are indicated in Fig. 41. In both processes the gas is compressed in a pump shown at the top and passed through a coil in *B* which is cooled with a refrigerant such as liquid ammonia, and then after further cooling in *C* and *D*, it is forced through a small opening *E* where it falls to atmospheric pressure. This large expansion causes a marked cooling and the cold gas passes up around the gas in the coils and cools them still further. This cooling of the incoming gas by the colder outgoing gas continues until finally the gas leaving the jet *E* is so cold that the additional cooling from expansion causes a part of it to liquefy and fall to the bottom of the container where it is drawn off and stored in vacuum-jacketed vessels.

The Linde process makes use only of the cooling due to this expansion of air against molecular attraction, and in spite of its extensive use it is inefficient from a theoretical standpoint. It operates at about 200 atm. and produces over half a liter of liquid air per horsepower-hour.

Instead of allowing the energy of compression to be wasted by free expansion into the atmosphere, as is done in the Linde process, the Claude process conserves some of it by passing a large fraction of the compressed gas through an engine *W*. The work done by this engine helps to operate the compressor *A* and so the total power consumption is reduced. After doing work in the engine *W*, the gas is colder and serves to cool further the rest of the gas which is passing

through the coils in chamber *C*. Still further cooling preparatory to expansion and liquefaction takes place in chamber *D*. Although this process is much more efficient than the one in which none of the energy of compression is recovered as useful work, there are practical

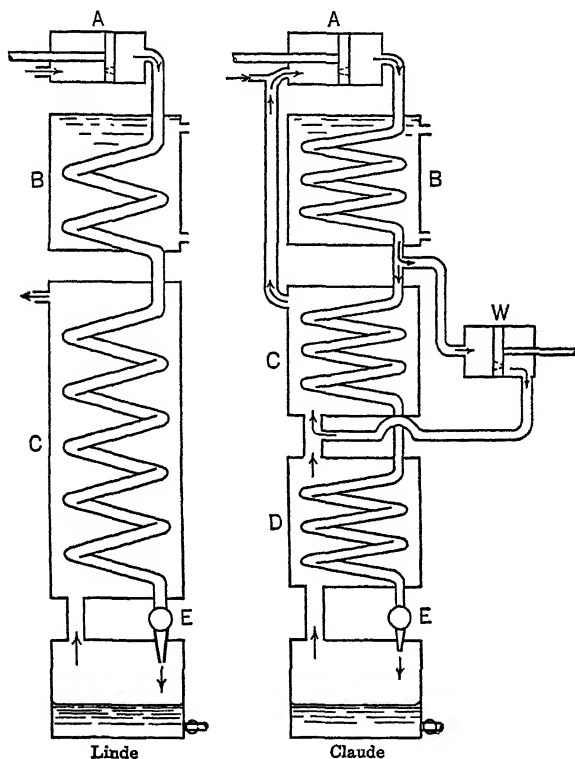


FIG. 41

difficulties in operating an expansion engine at low temperatures, because of the problem of lubrication and unequal thermal expansion of the moving parts.

The liquefaction of gases finds extensive application. Ammonia, sulfur dioxide, methyl chloride, and Freon ( $\text{CF}_2\text{Cl}_2$ ) are among the gases used in refrigeration. A gas suitable for refrigeration should have suitable boiling and freezing points, a high critical temperature, and a large heat of vaporization. It should be stable, non-poisonous, and inexpensive.

Solid carbon dioxide, known as "dry ice," is also much used as a refrigerant and as a substitute for ice. It is lighter than ice. It

leaves no water or objectionable residue on being heated, and it can be kept in small containers for several hours. When foods are frozen very rapidly by means of "dry ice" their texture is preserved. The increasing commercial use of dry ice makes available a convenient source of low temperature for laboratory experimentation. A vacuum bottle of dry ice in acetone gives a convenient mixture at about  $-80^{\circ}\text{C}$ .

Many gas mixtures can be separated by liquefaction. The fractional distillation of liquid air is the chief source of commercial nitrogen and oxygen. If the cost of liquefying air could be reduced, many new uses for oxygen would arise, particularly in blast furnaces and combustion operations involving the production of high temperatures. Oil-oxygen furnaces might replace electric furnaces, for example, in the production of calcium carbide.

The rare gases of the atmosphere, neon and argon used in electric lamps, can be recovered as by-products in the liquefaction of air. Formerly regarded as laboratory curiosities, they now find wide use in electric lighting — neon in high-voltage colored lights and signs, and argon in tungsten-filament lamps.

The removal of moisture from air by passage through tubes in a refrigerating bath, the recovery of helium from natural gas, and the production of liquid propane in tanks for household cooking are among the many industrial applications of the liquefaction of gases. The important laboratory investigations of specific heats at low temperatures are dependent on liquid air and liquid hydrogen.

**Vapor Pressure of Liquids.** According to the kinetic theory there is a continuous flight of molecules from the surface of a liquid into the free space above it. At the same time molecules of vapor return to the surface of the liquid at a rate depending on the concentration of the vapor. Eventually a condition of equilibrium is established between the liquid and its vapor, when the rate of escape is exactly equal to the rate of condensation of vapor. The vapor is then said to be *saturated*. The pressure exerted by vapor which is in equilibrium with the liquid is known as the *vapor pressure*. The equilibrium between a liquid and its vapor is dependent upon the temperature. For every temperature below the critical temperature, there is a certain pressure at which vapor and liquid may exist in equilibrium in all proportions; and, conversely, for every pressure below the critical pressure, there is a certain temperature at which vapor and liquid may exist in equilibrium in all proportions. This temperature is the standard boiling point of the liquid in the special case where the pressure is 760 mm. The vapor pressure of a liquid is a constant

quantity at any temperature and is independent of the amounts of liquid and vapor present but it increases as the temperature is raised. Table I gives the vapor pressures of several typical liquids from 0° to 100° C.

TABLE I  
VAPOR PRESSURES

Temp., °C.	Water	Acetic Acid	Ethyl Propionate	n-Hexane	Benzene
0	4 579	....	8.3	45.4	26 5
10	9 209	. . .	15 5	75 0	45 4
20	17.535	11 7	27.7	120 0	74.7
30	31 824	20 6	....	185 4	118.2
40	55 324	34 8	77.9	276.7	181.1
50	92 51	56.6	....	400 9	269.0
60	149.38	88.9	188.0	566 2	388.6
70	233.7	136 0	....	787 0	547.4
80	355.1	202 3	403.6	1062	754 4
90	525.76	293 7	....	1407	1016 1
100	760.00	417.1	785 0	1836	1344.3

The data of the foregoing table are represented in Fig. 42 plotted on rectangular coordinates, and in Fig. 43 where the logarithms of the vapor pressure are plotted against the reciprocals of the absolute temperature.

They all follow as a first approximation the equation

$$\log p = \frac{A}{T} + B \quad [1]$$

where  $p$  is the vapor pressure and  $A$  and  $B$  are constants.

*Example 1.* Draw the best straight line through the points obtained by plotting log vapor pressure of iodobenzene against the reciprocal of the absolute temperature. At 70° the vapor pressure is 13.65 mm., at 110° it is 73.88, and at 170° it is 479.7 mm.

(a) Find the equation for this straight line.

$$\log p = \frac{A}{T} + B$$

$$A = \text{slope} = -2.370 \times 10^3$$

$$B = y \text{ intercept} = 8.041$$

$$\log p = \frac{-2370}{T} + 8.041$$

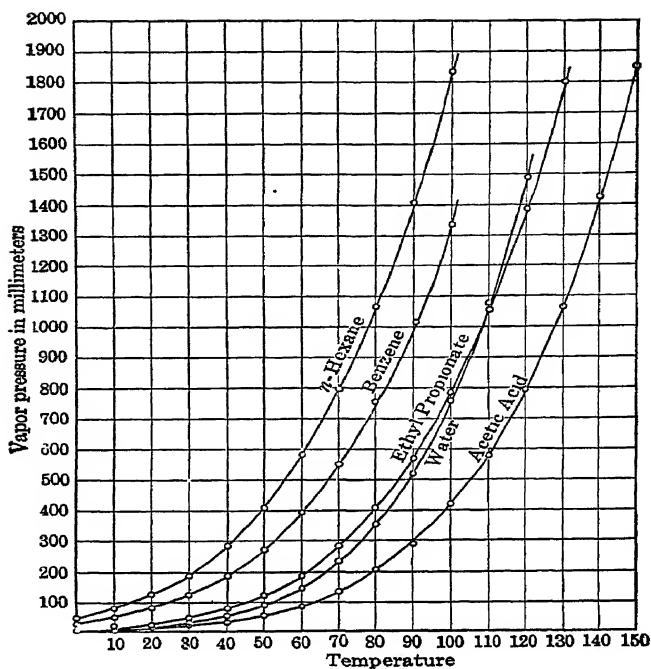


FIG. 42

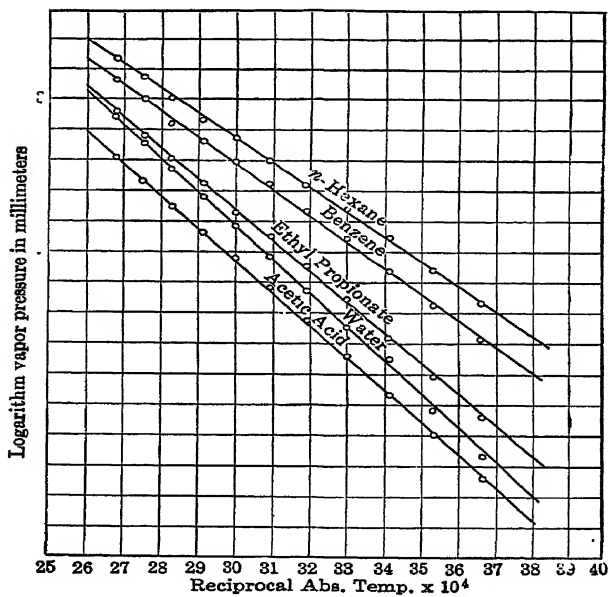


FIG. 43

(b) Calculate the vapor pressure at  $0^\circ$ .

$$\log p = \frac{-2370}{273.1} + 8.041 = -0.637; p = 0.231 \text{ mm.}$$

(c) Calculate the boiling point, i.e., the temperature at which the pressure is 760 mm.

$$\log 760 = \frac{-2370}{T} + 8.041$$

$$T = \frac{2370}{8.041 - \log 760} = 459.3^\circ \text{ K.} = 186.2^\circ \text{ C.}$$

**Measurement of Vapor Pressure.** The boiling temperatures of a liquid may be determined at various pressures using a pump to change the pressure and a manometer to measure it. The thermometer is not immersed in the liquid, because the liquid may become superheated. It is supported so that the vapor condenses on it and bathes the thermometer bulb with liquid, which is in equilibrium with the vapor at the measured pressure. In another method the liquid is allowed to drip slowly over the thermometer bulb while it is heated by the condensation of vapor. There is no danger of superheating the liquid above its normal boiling temperature if the heat is supplied only by the condensing vapor. Care must be taken to insure that all dissolved air or other gas is boiled out before the measurements are taken.

The *gas saturation method* is accurate and convenient for many purposes. A current of pure dry air or other gas is bubbled through or passed slowly through, a weighed amount of the liquid whose vapor pressure is to be determined. The liquid is maintained at constant temperature and its loss in weight is observed. The vapor may be removed from the gas stream in an absorption tube and weighed, or the liquid in the vessel may be weighed before and after. In passing through the saturating vessel the air absorbs an amount of vapor directly proportional to the vapor pressure of the liquid. A second bottle of the liquid gives better assurance that the air becomes saturated with the vapor. If  $v$  is the volume which contains  $g$  grams of the vapor (the vaporized liquid) having a molecular weight  $M$ , and  $p$  is the pressure of the vapor in equilibrium with the liquid at the temperature  $T$ , then the vapor pressure  $p$  of the liquid is calculated from the ideal gas laws by the formula,

$$pv = \frac{g}{M} RT$$

or

$$p = \frac{g}{Mv} RT \quad [2]$$



For approximate calculations the volume occupied by the vapor may be taken as the volume of the dry air measured before it becomes saturated with the vapor. For more accurate calculation or for high vapor pressures, allowance must be made for the fact that the total volume of the gases is increased by the introduction of the vapor so that the volume  $v$  through which the vapor molecules are distributed is  $v' \frac{P}{P - p}$  where  $v'$  is the volume of the pure air before saturation,  $P$  is the barometric pressure, and  $p$  is the vapor pressure of the liquid. Then

$$\begin{aligned} p &= \frac{g}{M} \frac{RT}{v} = \frac{g}{M} \frac{RT}{v'} \frac{P - p}{P} \\ p \left( 1 + \frac{g}{M} \frac{RT}{v'P} \right) &= \frac{g}{M} \frac{RT}{v'} \\ p &= \frac{gRT}{Mv'} \left/ \left( 1 + \frac{gRT}{Mv'P} \right) \right. \end{aligned} \quad [3]$$

*Example 2.* When liquid bromobenzene was vaporized at  $30.0^\circ$  by passing 20.00 liters of dry air through it the loss in weight of the liquid was 0.9414 g. The barometric pressure was 760 mm. The molecular weight is 157.0. Approximately what is the vapor pressure at this temperature?

$$p = \frac{g}{M} \frac{RT}{v} = \frac{0.9414 \times 0.08205 \times 303.1}{157.0 \times 20.00} = 0.00746 \text{ atm.}$$

$$p = 0.00746 \times 760 = 5.67 \text{ mm.}$$

More exactly what is the vapor pressure, using equation (3)?

$$p = 0.00746 \left/ \left( 1 + \frac{0.00746}{1} \right) \right. = 0.00740 \text{ atm.}$$

$$p = 0.00740 \times 760 = 5.62 \text{ mm.}$$

The difference between the use of equation (2) and equation (3) is much more pronounced with materials of high vapor pressure.

**The Clapeyron Equation.** The theoretical explanation of the empirical relation between vapor pressure and temperature was developed by Clapeyron in 1834. Consider a liquid in equilibrium with its vapor at a temperature  $T$  and a pressure equal to the vapor pressure  $p$  at that temperature. If some of the liquid is vaporized at this equilibrium pressure and temperature, by equation (35) of Chapter VII

$$\Delta F = 0$$

Since the free energy of the whole system does not change in this case, the decrease in free energy of the liquid phase due to the loss of a given weight of liquid, 1 g., for example, must equal the increase in free energy of the vapor phase due to the gain of 1 g. of vapor.

Representing the free energy of 1 g. of the liquid by  $F_1$ , and that of 1 g. of the vapor by  $F_2$  under these conditions, we may write for the previous equation

$$F_1 = F_2 \quad [4]$$

If the temperature is raised to  $T + dT$ , the pressure must be increased to  $p + dp$ , the vapor pressure at this higher temperature, in order for the two phases to be in equilibrium. Under these conditions the free energy of 1 g. of the liquid and of 1 g. of the vapor will be  $F_1 + dF_1$  and  $F_2 + dF_2$ , respectively, and since the change in free energy of the system must be zero for vaporization of the liquid at this equilibrium pressure and temperature

$$F_1 + dF_1 = F_2 + dF_2$$

Therefore, subtracting equation (4),

$$dF_1 = dF_2 \quad [5]$$

By differentiating equation (30) of Chapter VII

$$F_1 = E_1 + p_1 v_1 - T_1 S_1$$

we obtain

$$dF_1 = dE_1 + p_1 dv_1 + v_1 dp_1 - T_1 dS_1 - S_1 dT_1 \quad [6]$$

For a reversible process

$$dq = T dS$$

and by the first law of thermodynamics

$$dE_1 = dq - dw = T_1 dS_1 - p_1 dv_1$$

Substituting for  $dE_1$  in equation (6)

$$dF_1 = v_1 dp_1 - S_1 dT_1 \quad [7]$$

This relation gives the increase in free energy of 1 g. of the liquid when the pressure is increased by  $dp_1$  and the temperature by  $dT_1$ ;  $v_1$  is the volume and  $S_1$  the entropy of the given weight of liquid at pressure  $p_1$  and temperature  $T_1$ . A similar equation holds for the vapor

$$dF_2 = v_2 dp_2 - S_2 dT_2 \quad [8]$$

The subscripts on  $dp$  and  $dT$  may be dropped in equations (7) and (8) since the temperature and pressure of the two phases are the same. Using these equations and equation (5),

$$v_1 dp - S_1 dT = v_2 dp - S_2 dT$$

or on rearranging

$$\frac{dp}{dT} = \frac{S_2 - S_1}{v_2 - v_1} \quad [9]$$

Also we have

$$S_2 - S_1 = \frac{l}{T} \quad [10]$$

where  $l$  is the heat of vaporization of a gram of the liquid at this temperature and pressure. Substituting from (10) into (9) we obtain the Clapeyron equation

$$\frac{dp}{dT} = \frac{l}{T(v_2 - v_1)} \quad [11]$$

This equation gives the rate of change of the vapor pressure of a liquid with temperature,  $dp/dT$ , in terms of the heat of vaporization  $l$ , volume  $v_1$ , of the liquid, and volume  $v_2$  of the vapor at the temperature  $T$  and pressure  $p$ . The quantities  $l$ ,  $v_1$ , and  $v_2$  all apply to the same weight of material.

In using this equation it is necessary to have the units consistent, i.e., the heat term must be expressed in the same units as the product of pressure and volume change. If the pressure is given in atmospheres and volumes in milliliters, the heat may be expressed in milliliter-atmospheres (1 cal. = 41.29 ml.-atm.); or the pressure may be converted into dynes when the heat is expressed in ergs.

*Example 3.* What is the rate of change of the vapor pressure of water at 100° C.? The heat of vaporization is 539.7 cal. per gram, the specific volume, i.e., the volume occupied by 1 g., of liquid water is 1.043 ml., and the specific volume of steam, is 1677 ml., all at 100° C. and 1 atm.

$$\frac{dp}{dT} = \frac{539.7 \times 41.29}{373.1(1677 - 1.043)} = 0.0356 \text{ atm. per degree}$$

$$760 \times 0.0356 = 27.1 \text{ mm. per degree}$$

A formula of the same form as (11) may be obtained for the equilibrium between a solid and its vapor or between a pure solid and pure liquid. In the latter case  $dp/dT$  gives the change in pressure necessary to change the melting point by  $dT$ ;  $l$  represents the heat

of fusion per gram;  $v_2$  is the volume of a gram of the liquid; and  $v_1$  is the volume of the same weight of solid.

*Example 4.* Calculate the change in the freezing point of water produced by an increase in pressure of 1 atm. At  $0^\circ$  the heat of fusion of ice per gram is 79.7 cal. or 3291 ml.-atm., the density of water is 0.9998 g. per milliliter and the density of ice is 0.9168. The reciprocals of the densities, 1.0002 and 1.0908, are the specific volumes. For small changes in temperature we may replace  $dp/dT$  by  $\Delta p/\Delta T$ . Then

$$\frac{\Delta p}{\Delta T} = \frac{3291}{273.1(1.0002 - 1.0908)} = -133 \text{ atm. per degree}$$

In words, 133 atm. is the pressure required to lower the freezing point of water one degree; and the reciprocal

$$\frac{\Delta T}{\Delta p} = \frac{-1}{133} = -0.0075 \text{ degree per atmosphere}$$

shows that an increase in pressure of 1 atm. lowers the freezing point  $0.0075^\circ$ . The negative sign indicates that an increase of pressure causes a decrease in temperature, a relation which follows by Le Chatelier's theorem from the fact that the specific volume of ice is greater than that of water at the freezing point.

**The Clausius-Clapeyron Equation.** Clausius showed how the Clapeyron equation may be simplified by assuming that the vapor obeys the ideal gas law. Taking 1 mole instead of 1 g.,  $V_2$  is the volume of 1 mole of vapor,  $V_1$  is the volume of 1 mole in the liquid state, and  $L$  is the molar heat of vaporization (molecular weight  $\times l$ ). Furthermore,  $V_1$  may be considered negligible in comparison with  $V_2$ ; for example,  $V_1$  for water at  $100^\circ$  is 18.8 ml., and  $V_2$  is 30,200 ml. For  $V_2$  may be substituted its equivalent  $RT/p$ . Then

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)} = \frac{Lp}{RT^2}$$

On rearrangement this becomes

$$\frac{1}{dT} \frac{dp}{p} = \frac{L}{RT^2} \quad [12]$$

or

$$\frac{d \ln p}{dT} = \frac{L}{RT^2} \quad [13]$$

Since  $R$  is a constant, integrating on the assumption that  $L$  is a constant yields

$$\int d \ln p = \int \frac{L}{R} T^{-2} dT$$

$$\ln p = -\frac{L}{R} \frac{1}{T} + C \quad [14]$$

where  $C$  is the integration constant. This is the equation of a straight line, and when  $\ln p$  is plotted against  $1/T$  a straight line results, the slope of which is numerically equal to  $-L/R$ . When logarithms to the base 10 are plotted the slope is  $-L/2.303R$ . The theoretical justification for the empirical relation given in equation (1) is now apparent.

The slope of the line can be used for calculating the heat of vaporization, thus

$$L \text{ (in calories)} = -(\text{slope of line} \times 2.303 \times 1.987) \quad [15]$$

Frequently it is more convenient to use a formula obtained by integrating between limits,  $p_2$  at  $T_2$  and  $p_1$  at  $T_1$ , as follows:

$$\begin{aligned} \int_{p_1}^{p_2} d \ln p &= \int_{T_1}^{T_2} \frac{L}{R} T^{-2} dT \\ \ln p_2 - \ln p_1 &= \frac{L}{R} \left[ -\frac{1}{T_2} - \left( -\frac{1}{T_1} \right) \right] \\ \log \frac{p_2}{p_1} &= \frac{L(T_2 - T_1)}{2.303 \times 1.987 \times T_2 \times T_1} \end{aligned} \quad [16]$$

Using this equation it is possible to calculate the heat of vaporization from the vapor pressures at two different temperatures; and if the heat of vaporization and the vapor pressure at one temperature are known, the vapor pressure at any other temperature may be calculated. Any units of pressure and heat may be used as long as  $L$  and  $R$  are taken in the same units.

The unintegrated expression is most convenient in correcting boiling points for barometric fluctuations. For *small* changes in pressure the change in boiling point with pressure is given approximately by the formula

$$\frac{\Delta T}{\Delta p} = \frac{RT^2}{Lp} \quad [17]$$

Since this formula for calculating the heat of vaporization was derived on the assumption that the vapor behaved as a perfect gas, the results obtained by its use are no more accurate than the calculations involving the formula  $pv = nRT$ .

Another approximation is involved in the assumption of the constancy of the heat of vaporization. If the data are sufficiently exact and the temperature range sufficiently great it will be seen that the lines are not exactly straight. The lines would be straight if the heat capacities of the vapor and liquid were both the same and the vapor a

perfect gas. Under such conditions the heat of vaporization and the slope of the line would be constant. When the line is curved it is possible to determine the heat of vaporization at any temperature by drawing a tangent to the curve at that temperature. In general the slope of the  $\log p$  versus  $1/T$  line becomes steeper, i.e., the heat of vaporization becomes greater at the lower temperatures where more energy is required to pull the molecules apart and put them into the gas phase.

A more exact equation may be obtained by the addition of another term, thus

$$\log p = A/T + B \log T + \text{constant} \quad [18]$$

The vapor pressure of a large number of substances can be represented by this formula, even up to the critical temperature, with only small errors. The evaluation of the three constants from data at three temperatures by solving simultaneous equations requires accurate computations.

*Example 5.* If it is assumed that vapor follows the perfect gas law show that equation (18) can be derived from thermodynamics and state the physical significance of the constant  $B$ .

$$L = L_0 + \int (C_{\text{vapor}} - C_{\text{liquid}}) dT = L_0 + \Delta C_p \int dT = L_0 + \Delta C_p T$$

where  $L$  is the molar heat of vaporization at temperature  $T$ , and  $C_p$  is the heat capacity at constant pressure, which is independent of temperature. The constant  $L_0$  is a hypothetical heat of vaporization at absolute zero.

Substituting into equation (13)

$$\begin{aligned} \frac{d \ln p}{dT} &= \frac{L}{RT^2} = \frac{L_0 + (\Delta C_p)T}{RT^2} = \frac{L_0}{RT^2} + \frac{\Delta C_p}{RT} \\ \log p &= \frac{-L_0}{2.303RT} + \frac{\Delta C_p}{R} \log T + \text{constant} \end{aligned}$$

The constant  $B$  in equation (18) then is equal to the difference between the heat capacity of the vapor and liquid at constant pressure, divided by the gas constant. This conclusion is only an approximation because the deviations from the perfect gas laws still introduce an appreciable error which is not corrected in this derivation.

There are several useful relations of semi-empirical character which give the vapor pressures of liquids at different temperatures. It will be noted that in Fig. 43 the lines seem to be getting closer together at the higher temperatures, i.e., at the smaller values of  $1/T$ . An ideal-

ized graph is shown in Fig. 44 where all the liquids tend to come to a point at infinite temperature although of course the critical temperatures would be reached long before. At infinite temperature there

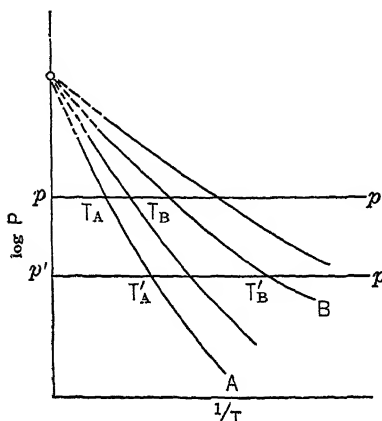


FIG. 44

would be no intermolecular forces and all the liquids would tend to behave alike and all gases would approach the ideal behavior. The different liquids have different heats of vaporization and hence different slopes but the lines are all of the same general character.

If one draws horizontal lines at two definite vapor pressures  $p'$  and  $p$  which are not too far apart, there is a rough proportionality in the temperatures, as one would expect from the intersection of parallel lines on a series of lines whose slopes, representing the heats

of vaporization, are of the same order of magnitude. Thus the vapor pressure  $p$  is reached by liquid  $A$  at temperature  $T_A$  and by liquid  $B$  at  $T_B$ ;  $p'$  is reached by liquid  $A$  at  $T'_A$  and by liquid  $B$  at  $T'_B$ . Then

$$\frac{T_B}{T'_B} \approx \frac{T_A}{T'_A}$$

or

$$T_B \approx \frac{T'_B}{T'_A} T_A$$

This relation is known as Duhring's rule and it is useful for estimating approximately the vapor pressures at various temperatures for any liquid  $B$  if the vapor-pressure temperature data are available for a reference liquid  $A$ .

*Example 6.* Benzene boils at  $80^\circ$  and  $n$ -hexane at  $69^\circ$ . Benzene has a vapor pressure of 74.7 mm. at  $20^\circ$ . At what temperature does  $n$ -hexane have a vapor pressure of 74.7 mm.?

$$T_{n\text{-hexane, 74.7 mm.}} = \frac{342}{353} \times 293 = 284^\circ \text{ K.} = 11^\circ \text{ C.}$$

The experimentally determined temperature is  $10^\circ$  (Table I).

The same principle can be applied in estimating solubilities and several other physical chemical properties which show a straight-line

relationship when the logarithm of the property is plotted against the reciprocal of the absolute temperature.

Graphical methods making use of Duhring's rule are available. The vapor-pressure curve of one reference liquid must be known. Rather exact vapor-pressure relations which are useful for industrial work particularly in the distillation of petroleum, have been reviewed and developed by Watson.\*

A practical nomograph is available† for correcting boiling points for pressure with an accuracy of  $0.25^\circ$  or 2 mm. pressure. A straight-edge is laid across two scales and across a point which is located for each liquid. These points, dependent in a theoretical way on the heats of vaporization, are located for nearly two hundred organic liquids and new points for other liquids can be located when vapor-pressure data are available.

Other simpler empirical rules for boiling-point corrections depend on the Clapeyron equation and on Trouton's rule discussed in the following section.

#### Empirical Vapor Relationships.

If the densities of a liquid and its saturated vapor are plotted against temperature, a curve of the form shown in Fig. 45‡ is obtained. The density of the liquid becomes less at the higher temperatures, but the density of the vapor becomes greater. The higher vapor pressure is responsible for the increased vapor density. The two densities approach each other and become equal at the

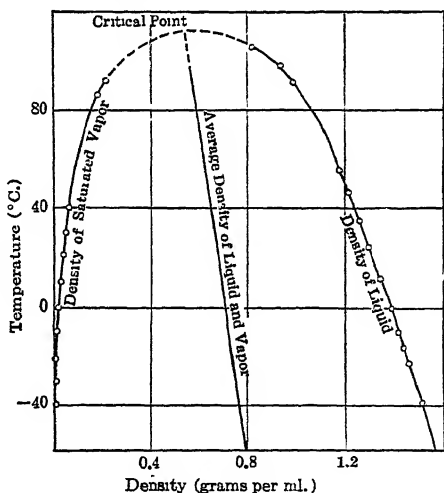


FIG. 45

critical temperature. The mean of the densities of any substance in the liquid and vapor states, when plotted against the corresponding temperature, lie on a straight line. If  $d_l$  and  $d_v$  denote the densities of liquid and vapor, respectively, this approximate relation pointed out by Cailletet and Mathias may be expressed mathematically

\* Watson, *Ind. Eng. Chem.*, **23**, 360 (1931).

† Germann and Knight, *Ind. Eng. Chem.*, **26**, 467 (1934).

‡ From measurements of Bichowsky and Gilkey on  $\text{CCl}_2\text{F}_2$ , *Ind. Eng. Chem.*, **23**, 365 (1931)



cally by the equation

$$\frac{d_i + d_o}{2} = A + BT \quad [19]$$

where  $A$  and  $B$  are constants. The relation is useful in determining the value of the critical density, a quantity which frequently cannot be measured directly.

A rough relationship is given in Table III of Chapter II, where it is seen that the standard boiling point (i.e., the temperature at which the vapor pressure becomes equal to 1 atm.) is equal in many cases to about 0.6 or two-thirds of the critical temperature both expressed in absolute temperatures. In this way a very approximate estimate of the critical temperature can be obtained from the boiling point of a given liquid.

In order to transform a liquid into a vapor, a large amount of heat is required. When a liquid is vaporized at the boiling point, some work must be done when the volume is increased against the pressure of the atmosphere, but much more energy is expended in overcoming the attraction between the molecules themselves.

According to Trouton's approximate relation, if  $T$  denotes the absolute boiling point, and  $L$  the heat of vaporization of 1 mole of liquid, then

$$\frac{L}{T} = 21 \quad [20]$$

In words, the ratio of the molar heat of vaporization to the absolute boiling temperature of a liquid is constant, approximately 21. The relation is shown over a wide range of temperature in Table II.

Water, alcohols, ammonia, and other substances with large dipole moments (page 81) have a strong dipole attraction between molecules and require an extra amount of energy for separation of the molecules into the gas phase. Hydrogen and helium, which boil only a little above absolute zero, would not be expected to follow this rule. Acetic acid and carboxylic acids in general are abnormal in that the vapor consists of double molecules.

It will be realized that Trouton's empirical rule has a theoretical backing somewhat as follows. As in many physical chemical properties the magnitude of the property is more significant on the molar basis than on the gram basis. The molar heat of vaporization divided by the absolute temperature is the entropy of vaporization (page 130). The change from a liquid to a vapor involves a change toward increasing disorder, i.e., more random motion, and it is meas-

TABLE II  
HEATS OF VAPORIZATION

	Boiling Temp. °C.	Cal./ Gram	L/T		Boiling Temp. °C.	Cal./ Gram	L/T
CH <sub>4</sub> .....	-161.4	138.2	19.8	H <sub>2</sub> O.....	100.0	539.7	26.1
HCl.....	-85.0	98.7	19.2	H <sub>2</sub> S.....	-59.6	132.	21.1
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O....	34.6	83.9	20.2	NH <sub>3</sub> .....	-33.4	327.	23.4
CHCl <sub>3</sub> .....	61.5	59.0	21.0	HF.....	17.	361.	24.9
CCl <sub>4</sub> .....	76.7	46.5	20.4	CH <sub>3</sub> OH... .	64.7	263.	24.9
C <sub>6</sub> H <sub>6</sub> .....	80.2	94.4	20.8	C <sub>2</sub> H <sub>5</sub> OH... .	78.5	204.	26.6
SnCl <sub>4</sub> .....	112.	30.4	20.5	He.....	-268.9	6	5.7
C <sub>10</sub> H <sub>22</sub> .....	160.	60.2	19.8	H <sub>2</sub> .....	-252.7	108.	10.6
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> ....	210	79.1	20.1	CH <sub>3</sub> COOH..	118.1	96.8	14.8
C <sub>10</sub> H <sub>8</sub> .....	218.	75.5	19.7	.....	.....	.....	.....

ured quantitatively by the entropy of vaporization. At the critical temperatures, the entropy of vaporization of all normal liquids is probably the same. The boiling points at atmospheric pressure are roughly two-thirds of the critical temperature and according to the reduced equation of state they would be expected to have the same general relationships as at the critical temperature, i.e., the entropies of all liquids should be about the same at their boiling points.

When, in addition to the normal force of attraction causing the vaporized material to liquefy, there are other forces which hold molecules tightly together in the liquid state the heat of vaporization becomes abnormally large.

*Example 7.* The boiling point of *n*-heptane is 98°. Estimate (a) the heat of vaporization per gram and (b) the critical temperature ( $M$  = molecular weight).

$$(a) \frac{L}{M} = \frac{21T}{M} = \frac{21 \times (273 + 98)}{100} = 77.9$$

$$(b) T_c = \frac{3}{2} T_b = \frac{3 \times 371}{2} = 557. \quad t_c = 284$$

The experimentally determined heat of vaporization is 76.4 cal. per gram and the critical temperature is 266°.

**Surface Tension.** The attraction between the molecules of a liquid manifests itself near the surface where the molecules are subject to an unbalanced force. The molecules at the surface are pulled inward by the other molecules of the liquid and the liquid tends to adjust itself to give the minimum surface area. This fact explains

many common phenomena, including the spherical shape of rain-drops, the rise of water in a capillary tube, and the movement of water in blotting paper or in the soil. The surface tension of a liquid,  $\gamma$ , is the force per centimeter on the surface of a liquid which opposes the expansion of the surface area. This definition is illustrated in **Fig. 46** where the force  $f$  is pulling on a movable bar against a liquid film which is stretched like a soap-bubble film on a wire frame. Then

$$\gamma = \frac{f}{2l} \quad [21]$$

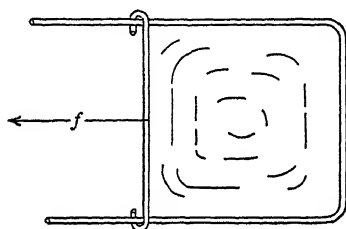


FIG. 46

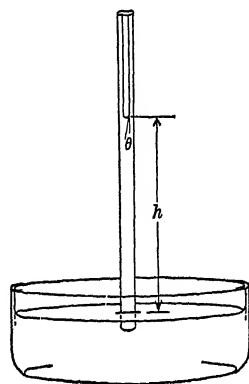


FIG. 47

where  $l$  is the length of the bar in centimeters, and the factor 2 is introduced because there are two liquid surfaces, one at the front and one at the back.

Some liquids, like water, wet the walls of a glass capillary tube, whereas others, like mercury, do not. When a liquid wets the tube, the liquid adhering to the walls pulls the body of the liquid up, but when the liquid does not adhere, the liquid is depressed. In the first instance the surface of the liquid in the tube is concave. In the second it is convex.

The most accurate method for determining the surface tension of a liquid consists in measuring the height to which it rises in a capillary tube.

A capillary tube of radius  $r$ , as shown in **Fig. 47** is immersed in a vessel of liquid whose density is  $d$ . The liquid wets the tube and the liquid rises. It continues to rise until the surface tension tending to pull the liquid upward is counterbalanced by the force of gravity pulling it downward. The height to which the liquid rises at this equilibrium point is denoted by  $h$ . The downward force exerted by the column of liquid in the capillary tube is  $\pi r^2 h d g$ , where  $g$  is the acceleration due to gravity. The force sustaining this weight is the vertical component,  $2\pi r \gamma \cos \theta$ , of the force due to the tension of the

liquid surface at the walls of the tube,  $\gamma$  being the surface tension and  $\theta$  the angle of contact of the liquid surface with the walls of the tube. Therefore

$$\pi r^2 h d g = 2 \pi r \gamma \cos \theta \quad [22]$$

or 
$$\gamma = \frac{h d g r}{2 \cos \theta}$$

For water and many other liquids  $\theta$  is so small, particularly when the glass is scrupulously clean, that as an approximation  $\theta = 0$ , and  $\cos \theta = 1$ . The foregoing expression becomes

$$\gamma = \frac{1}{2} h d g r \quad [23]$$

Thus the surface tension of a liquid can be calculated, provided its density and the height to which it rises in a previously calibrated tube are known. When  $h$  and  $r$  are expressed in centimeters,  $\gamma$  will be expressed in dynes per centimeter or ergs per square centimeter.

Surface tension can be measured quantitatively by various other means, including the pulling of a wire ring away from the surface of a liquid, the weighing of drops which fall from a special glass tip, and the reflection of light from ripples on the surface of a liquid. When the liquid is in contact not with air or with its own vapor but with an immiscible liquid, the interfacial tension may be quite different. This property is important in colloid chemistry.

**Surface Tension and Temperature.** The surface tension of a liquid decreases as the temperature rises and the molecular agitation increases. At the critical temperature, where the liquid becomes indistinguishable from a gas, the surface tension should become negligible. The following quantitative relation was developed by Eötvös and by Ramsay and Shields

$$\gamma(Mv)^{2/3} = k(t_c - 6 - t) \quad [24]$$

where  $Mv$  is the volume of a mole of the liquid,  $t$  is the temperature of the experiment,  $t_c$  is the critical temperature, and  $k$  is a constant independent of temperature or the nature of the liquid.  $M$  is the molecular weight and  $v$  is the volume of 1 g.

The constant 6 is an empirical constant introduced to give values in better agreement with the experimental values. It is claimed by

some to have theoretical significance. The two-thirds power comes from the fact that the surface  $s$  of a sphere is proportional to the square of the radius  $r$  whereas the volume  $v$  is proportional to the cube of the radius.

$$\frac{v_1}{v_2} = \frac{r_1^3}{r_2^3}; \quad \frac{s_1}{s_2} = \frac{r_1^2}{r_2^2}$$

hence

$$\frac{s_1}{s_2} = \frac{v_1^{2/3}}{v_2^{2/3}} \quad [25]$$

Taking  $M$  as the molecular weight determined in the gas phase, the value of  $k$  in equation (24) is found to be of the order of 2.12. This value holds for a large number of nonpolar liquids, such as carbon tetrachloride, benzene, and many organic substances. For certain other liquids, such as water or the alcohols or acetic acid, and polar liquids in general,  $k$  is found to have a value considerably less than 2.12. The same liquids which have abnormal surface tensions possess heats of vaporization larger than are calculated by Trouton's law. They are polar compounds with large dipole moments which possess abnormalities in several properties. The surface tensions of a few common liquids, measured in air, at different temperatures are shown in Table III.

TABLE III  
SURFACE TENSION OF LIQUIDS IN DYNES PER CENTIMETER

Temp. °C.	H <sub>2</sub> O	CCl <sub>4</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> OH
0	75.6	29.0	31.6	46.4	24.0
25	71.8	26.1	28.2	43.2	21.8
50	67.9	23.1	25.0	40.2	19.8
75	63.5	20.2	21.9	37.3	....

**Viscosity.** The resistance experienced by one portion of a liquid in moving over another portion is called *viscosity*. The viscosity of liquids varies greatly, some liquids, such as ether, being very mobile, while others, such as tar, are extremely viscous. It has been shown experimentally that the tangential force,  $f$ , required to maintain a constant difference between the velocities of two parallel layers of liquid moving in the same direction varies directly with the difference in velocity,  $u$ , and the area,  $A$ , of the surface of contact of the two

layers, and inversely as the distance,  $s$ , between the layers. That is,

$$f = \eta \frac{Au}{s} \quad [26]$$

where  $\eta$  is a proportionality factor known as the *coefficient of viscosity*. The unit of viscosity is the *poise*; it is the viscosity of a hypothetical liquid such that a force of one dyne causes two parallel liquid surfaces one square centimeter in area and one centimeter apart to slide past one another with a velocity of one centimeter per second. The force required to produce this effect is considerably less than one dyne for ordinary liquids; water, for example, has a viscosity of 0.00895 poise at 25°.

The viscosity of a liquid is generally measured by observing the time required for a definite volume of liquid to flow through a standardized capillary tube under a known difference of pressure. An instrument for measuring viscosities is called a *viscometer*. The law governing the flow of liquids through capillary tubes was discovered by Poiseuille; it may be expressed by the equation

$$\eta = \frac{\pi P r^4}{8vl} t \quad [27]$$

in which  $v$  denotes the volume of liquid of viscosity  $\eta$ , flowing through a capillary tube of length  $l$  and radius  $r$ , in the time  $t$  and under the pressure difference  $P$ .\*

If the times of flow of equal volumes of two liquids through the same capillary are measured under the same head of liquid, it follows from equation (27) that

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad [28]$$

where  $\eta_1$  and  $\eta_2$  denote the coefficients of viscosity of the two liquids,  $d_1$  and  $d_2$  their densities, and  $t_1$  and  $t_2$  their times of flow. If a liquid of known viscosity is selected as a standard, equation (28) may be used to calculate the so-called "relative viscosity" of other liquids. Water is quite generally accepted as the standard of reference in determinations of relative viscosity. In calculating the relative viscosity of a liquid referred to water, the following equation is used:

$$\frac{\eta_1}{1} = \frac{d_1 t_1}{d_w t_w} \quad [29]$$

\* The derivation of this equation is given in specialized texts such as Barr's "A Monograph on Viscometry," Oxford University Press, Oxford, 1931.

the symbols  $\eta_1$ ,  $d_1$ , and  $t_1$  denoting the viscosity, density, and time of flow, respectively, of the liquid under investigation, and  $d_w$  and  $t_w$  the density and time of flow of water. Relative viscosities may be transformed into absolute viscosities by multiplying the relative viscosity by the absolute viscosity of water at the same temperature.

The viscosity of a liquid may be determined not only by measuring the time required for a liquid to flow through a capillary tube but also by measuring the time required for a heavy sphere (ball bearing) to fall through a liquid. Or two disks may be placed in the liquid and measurements made on the torsional force produced on one by the rotation of the other; or the time required for a liquid in a cup to run out through a small hole in the bottom may be determined. These methods are indicated in Fig. 48.

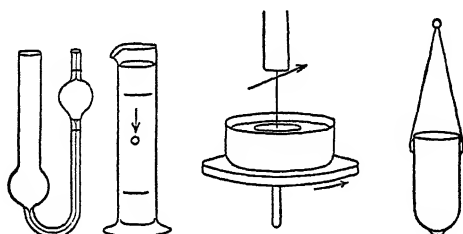


FIG. 48

The viscosity of liquids has been found to decrease about 2 per cent for each degree rise in temperature. Increase of pressure, on the other hand, causes the viscosity of liquids to increase, the change in viscosity being greater at higher pressures than at low. The viscosities of a few liquids at different temperatures are shown in Table IV.

TABLE IV  
VIScosity OF LIQUIDS IN POISES

	0°	25°	50°	75°
Water	0 01793	0 00895	0 00549	0 00380
Ethanol	0.0179	0 0109	0 00698	.....
Benzene	0 0090	0 0061	0 0044	.....

The viscosity of a *perfect* fluid would increase as the temperature increases. Viscosities of actual liquids decrease. This fact suggests that the passage of one layer of liquid across another involves the migration from one large group of molecules to another. There is other evidence, too, for the existence of molecular clustering in liquids.

The temperature effect on viscosity permits a calculation of the energy required for molecules to break away from these groups. Attempts have been made to treat the matter mathematically.

An empirical relation exists as follows

$$\log \eta = \frac{A}{T} + B \quad [30]$$

where  $A$  and  $B$  are constants.

The reciprocal of viscosity is called fluidity;  $\phi = 1/\eta$ . Fluidity may be regarded as the measure of the tendency of a liquid to flow, whereas viscosity is a measure of the resistance which a liquid offers to flowing.

The fluidities of mixtures of nonpolar liquids are in general additive. Thus

$$\phi = m\phi_1 + n\phi_2 \quad [31]$$

where  $m$  and  $n$  are the volume fractions of the two liquids.

The viscosities of mixtures of associated liquids or liquids which exhibit some interaction may give widely varying viscosities, mixtures of some liquids having viscosities greater than either pure liquid alone.

Viscosity is an important property in both practical and theoretical work. In biology and physiology the viscometer has become an almost indispensable instrument for the study of the properties of blood and other animal fluids, and in the realm of technology it has been applied successfully to the solution of a wide variety of problems presented by the paint, rubber, glue, textile, and other industries.

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#### PROBLEMS

1. Propene has the following vapor pressures at the following absolute temperatures:

$T$ (°K.)	150	200	250	300
$P$ (mm.)	3.82	198.0	2,074	10,040

Graph these data so as to obtain a nearly straight line and determine the vapor pressure at 225° K.

*Ans.* 738.



2. A liquid whose density is 0.85 was found to rise to a height of 50 cm. in an evacuated barometer tube when the barometric pressure was 740 mm. of mercury. What is the vapor pressure of the liquid? *Ans.* 708.7 mm.

3. A room 6 by 12 by 4 meters is filled with air containing some water vapor. The temperature is 20° and the relative humidity is 60 per cent. The vapor pressure of water at 20° is 17.36 mm. (The relative humidity is the partial pressure of water vapor divided by the vapor pressure of the liquid water.) How many grams of water are contained in the air of this room? *Ans.* 2954 g.

4. The heat of vaporization of ether is 88.39 cal. per g. at its boiling point, 34.5°.

(a) Calculate the rate of change of vapor pressure with temperature  $dp/dT$ , near the boiling point.

(b) What is the boiling point at 750 mm.?

(c) What is the vapor pressure at 36.0°?

*Ans.* (a) 26.47 mm. per degree (b) 34.12°. (c) 799.7 mm.

5. Acetic acid melts at 16.6°,  $dT/dp = 0.0242^\circ$  per atmosphere, and the heat of fusion is 46.42 cal. per g. Calculate the change in volume accompanying the liquefaction of 1 g. of acid. *Ans.* 0.160.

6. Methanol has a surface tension of 22.6 dynes per cm. and a density of 0.79 at 20°. What is the radius of the largest capillary which will permit the liquid to rise 1.5 cm.? *Ans.* 0.0389 cm.

7. Heptane flows through a viscometer in 83.8 sec., and the same volume of water under the same conditions requires 142.3 sec. Calculate the relative viscosity and the absolute viscosity of heptane at 20°. The density of heptane at 20° is 0.689 and that of water is 1.000. The viscosity of water at 20° is 0.01009.

*Ans.* 0.00410.

8. Ten liters of air was bubbled through carbon tetrachloride at 20°. The loss in weight of the liquid was 8.698 g. Calculate the vapor pressure of carbon tetrachloride by the approximate formula (2) and by the more exact formula (3).

9. Estimate the vapor pressure of nitrobenzene at 25° from the fact that the standard boiling point is 210° and the heat of vaporization 79.1 cal. per g.

10. A block of ice is placed in a lake of pure water, forced 100 ft. below the surface, and maintained in a quiet, steady position. What will be the temperature of the surface of the ice? Assume that the densities of the ice and water are not changed by the pressure. At atmospheric pressure the melting point of ice is 0°. The densities of ice and water are 0.9106 and 1.000 respectively.

11. From the data of the tables given in this chapter estimate the temperature at which methanol has a vapor pressure of 92.5 mm.

12. The standard boiling point of ethanolamine is 172.2°. The molecular weight is 61.06.

(a) Estimate the heat necessary to vaporize 100 g. of ethanolamine.

(b) Estimate the critical temperature.

13. The densities of vapor and liquid methyl ether at various temperatures are as follows:

$t$	30°	50°	70°	100°	120°
$d_v$	0.6455	0.6116	0.5735	0.4950	0.4040
$d_w$	0.0142	0.0241	0.0385	0.0810	0.1465

If the critical temperature of this substance is 126.9°, what is its critical volume?

14. Acetone has a density of 0.790 and rises to a height of 2.56 cm. in a capillary tube having a radius of 0.0235 cm. What is the surface tension of the acetone at this temperature?

15. If it takes 10 minutes to drain a capillary pipet at 25° when filled with water, how long will it take to drain it when it is filled with ethanol (density = 0.789)?

16. In an industrial operation 10,000 cu. ft. of air is blown through a chamber per minute. The air at 25° and 40 per cent relative humidity is dried by removal of the water in an adsorbing agent. Calculate how many kilocalories of heat will be required per hour to regenerate the adsorbing agent by evaporating the water (582 cal. per g.). The vapor pressure of water at 25° is 23.7 mm.

17. What is the boiling point of water on a mountain where the barometer reading is 500 mm.?

18. At 0° ice absorbs 80 cal. per g. in melting; water absorbs 597 cal. in vaporizing.

(a) What is the heat of sublimation of ice at this temperature?

(b) At 0° the vapor pressure of both ice and water is 4.6 mm. What is the rate of change of vapor pressure with temperature  $\left(\frac{dp}{dT}\right)$  for ice at this temperature?

(c) Estimate the vapor pressure of ice and of liquid water at -5°.

19. The boiling point of *n*-butyl chloride is 77.96°.

(a) Using this as the only experimental datum available, calculate the vapor pressure at 50° and compare with that calculated from the empirically determined equation (in which  $p$  is expressed in cm.)

$$\log p = -\frac{1763}{T} + 6.912$$

(b) Calculate the heat of vaporization per gram.

20. The vapor pressures of benzene are 74.7 and 269.0 at 20° and 50° respectively. Compare the heats of vaporization as calculated by the approximate equation using increments, with the more exact values obtained by integration.

21. Estimate the critical temperature of benzene from the surface tension data. The density of benzene at 25° is 0.879.

22. Plot log of viscosity of mercury against the reciprocal of the absolute temperature for the following data and estimate the viscosity of mercury at 50°.

$t$	0°	20°	35°	98°	203°
$\eta$	0.01661	0.01547	0.01476	0.01263	0.01079

23. A certain liquid boils under atmospheric pressure (760 mm.) at  $t^\circ$ . Estimate: (a) the critical temperature of the substance, (b) the heat of vaporization of liquid, (c) its boiling point at 720 mm. pressure. How accurate would you expect these estimates to be?

24. Using the equation defining viscosity, determine the dimensions of viscosity in terms of the fundamental units of mass, length, and time.

25. Plot the logarithm of the vapor pressure of mercury against  $1/T$  for values of  $T$  between 0° and 360° (from reference tables) and draw tangents at two different temperatures. Show that the heat of vaporization changes with the temperature. If mercury vapor is monatomic what can be stated regarding the specific heat of liquid mercury?

26. The vapor pressure of 2,2-dimethylbutanol is given by the expression:

$$\log p = \frac{-4849.3}{T} - 14.701 \log T + 53.1187$$

where  $p$  is expressed in millimeters of Hg. Calculate the heat of vaporization (a) at 25°, (b) at the boiling point, 136.7°.

27. Mercury does not wet a glass surface. Draw a figure analogous to Fig. 47 (page 164) for mercury and glass and calculate the relative positions of the mercury surfaces, if the diameter of the capillary is 0.1 mm. The density of mercury is 13.5 g./ml. The surface tension of mercury is 520 dynes per cm.

28. For *n*-hexane the boiling point is 69.0° and the density is 0.660. Estimate, from relationships in this chapter, the surface tension of *n*-hexane at 20°.

## CHAPTER IX

### SOLUTIONS

A solution may be defined as a system of two or more chemical substances which has the same chemical composition and physical properties in every part. Thus the addition of alcohol to water produces a homogeneous, single-phase system composed of two different chemical substances uniformly and intimately mixed with each other.

When one substance is dissolved, or molecularly dispersed, in another, it is customary to designate as the *solvent* that component which is present in the larger proportion, and to call the other component the *solute*. This designation is purely arbitrary, particularly when two liquids are miscible in all proportions. Under such conditions either one may be regarded as the solvent.

The quantitative prediction of solubility on the basis of physical properties of the solute and solvent is possible for only a limited number of solutions. In general, it can be stated that similar substances like benzene and toluene or alcohol and water will dissolve in each other, as well as substances which tend to interact chemically. For example, the hydration of the ions provides the necessary energy for breaking apart the crystal lattice of salts in water. Substances which are not alike or which do not combine chemically generally are not very soluble in each other. For example, hydrocarbons and fats as a rule are insoluble in water but soluble in organic solvents.

**The Composition of Solutions.** There are several different ways in which the composition of a solution may be expressed. Each has advantages for particular purposes.

Volume concentrations are used in volumetric analysis because it is convenient to introduce with each milliliter of solution a definite number of molecules. A *molar solution* contains 1 mole of solute in a liter of solution. A *normal solution* contains an equivalent weight in a liter of solution, but it is necessary to specify whether the solution is normal with respect to neutralization or oxidation or other reaction.

Weight concentrations are used in physical chemistry because they are uninfluenced by temperature, whereas the volume concentrations are subject to variations caused by changes in density. A *molal solution* contains 1 mole of solute dissolved in 1000 g. of solvent. The

term "molal" and symbol " $m$ " usually refer to weight concentrations whereas the term "molar" and symbol " $M$ " usually refer to volume concentrations. One may be converted into the other when the density of the solution is known.

*Mole fractions* are used in theoretical work because many physical properties of solutions are expressed most simply in terms of the relative numbers of molecules. The mole fraction of a dissolved substance is defined as the number of moles of the substance divided by the total number of moles. Thus, if a solution is composed of  $n_A$  moles of  $A$  and  $n_B$  moles of  $B$ , the mole fractions of the two components will be as follows:

$$\text{Mole fraction of } A = N_A = \frac{n_A}{n_A + n_B} \quad [1]$$

$$\text{Mole fraction of } B = N_B = \frac{n_B}{n_A + n_B} \quad [2]$$

It is obvious that the mole fraction of  $A$  plus the mole fraction of  $B$  must be equal to 1. If three or more different substances are involved, the denominator always contains the total number of moles of all kinds.

Percentage by weight is often used in technical work to express the composition of a solution.

*Example 1.* Illustrate the four different ways in which concentrations of solutions can be expressed using a solution containing 1 mole of ethanol (46 g.) in 1000 g. of water, the density of the solution being 0.992.

*Weight concentration:*

$$\frac{1 \text{ mole}}{1000 \text{ g.}} \times 1000 = 1 \text{ molal}$$

*Volume concentration:*

$$\frac{\frac{1 \text{ mole}}{1000 + 46}}{0.992} \times 1000 = 0.948 \text{ molar}$$

*Mole fractions:*

$$\text{Mole fraction H}_2\text{O} = N_1 = \frac{\frac{1000}{18}}{\frac{1000}{18} + 1} = 0.982$$

$$\text{Mole fraction C}_2\text{H}_5\text{OH} = N_2 = \frac{1}{\frac{1000}{18} + 1} = 0.018$$

Percentage by weight:

$$\text{Percentage H}_2\text{O} = \frac{1000}{1046} \times 100 = 95.6$$

$$\text{Percentage C}_2\text{H}_5\text{OH} = \frac{46}{1046} \times 100 = 4.4$$

**Solutions of Gases in Gases.** This constitutes the simplest case of a solution. The components may be present in any proportions since gases are completely miscible. In a mixture of gases where no chemical action occurs, each gas behaves independently, the properties of the gaseous mixture being the sum of the properties of the constituents. Thus, *the total pressure of a mixture of several gases is equal to the sum of the pressures which each gas would exert were it alone present in the volume occupied by the mixture.* This law was discovered by Dalton and is known as *Dalton's law of partial pressures.* If the partial pressures of the constituent gases are denoted by  $p_1, p_2, p_3$ , etc., and  $p$  and  $v$  represent the total pressure and the total volume of the gaseous mixture, then

$$pv = v(p_1 + p_2 + p_3 + \dots) \quad [3]$$

Dalton's law holds when the partial pressures are not too great, its order of validity being the same as that of the other gas laws. Dalton's law can be tested experimentally by comparing the total pressure of the gases with the sum of the pressures exerted by each gas before mixture.

An experimental verification of Dalton's law was carried out by Ramsay with a mixture of nitrogen and hydrogen using a thin-walled, heated palladium vessel containing nitrogen set in a large vessel containing hydrogen. The general principle is shown in Fig. 49. Hydrogen can pass through hot palladium but nitrogen cannot. The pressure of nitrogen was determined with a mercury manometer and when hydrogen was admitted to the outer vessel it passed through the wall to establish equal pressures of hydrogen inside and outside. The

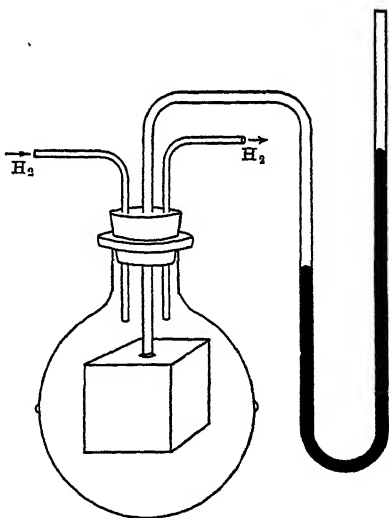


FIG. 49

manometer showed that the total pressure inside the palladium vessel, in conformity with Dalton's law, increased from the original pressure of the nitrogen to a total pressure equal to the pressure of the nitrogen plus the pressure of the hydrogen.

It would not be expected that this law would be any more accurate than the simple gas law. Data regarding deviations from Dalton's law have been very meager.

Edwards and Roseveare\* measured the following volume changes at 25° and 1 atm. when 3174 ml. of the first gas was mixed with 3421 ml. of the second gas and the pressure was readjusted to 1 atm.: nitrogen + hydrogen increased 1.23 ml.; carbon dioxide + hydrogen increased 2.14 ml.; and ethylene + hydrogen increased 2.94 ml.

These changes in volume provide interesting material for the direct calculation of the inter-attraction between molecules in one of the simplest possible chemical systems.

**Ideal and Non-Ideal Solutions.** It has been shown that an ideal gas is one in which there is no attraction between the molecules and no change in internal energy when the volume is changed. Similarly an ideal solution is one in which no special force of attraction exists between the components of the solution and no change in internal energy is produced on mixing. Under these conditions no change in the character of liquids is produced by mixing, merely a dilution of one liquid by the other. When two liquids are mixed to give an ideal solution, there is no heat effect and the properties are strictly additive. The volume of the solution is the sum of the volumes of the two liquids, and there is no more shrinkage or expansion than when two different samples of the same liquid are mixed. Other physical properties of the solution, such as refractive index, fluidity, and vapor pressure, can be calculated directly by averaging the properties of the components which make up the solution.

One of the most fundamental properties of a substance is the tendency for its molecules to pass into the surrounding space. It is manifest, for example, in the vapor pressure of a liquid or solid and in solubility. In solutions this escaping tendency describes accurately the activity of the substance when surrounded by the other molecules. It is measured directly as the partial vapor pressure. Thus measurement of vapor pressure is of considerable importance in the study of solutions.

The vapor pressure of a pure liquid depends on the rate of escape of molecules from the surface of the liquid, and when the liquid is mixed with another liquid, the concentration in the surface is decreased and

\* Forthcoming publication.

the rate of escape diminished. Moreover, in an ideal solution, where the character of the liquid remains unchanged, the partial vapor pressure of one component is directly proportional to the number of molecules of that component in the mixture. In other words

$$p_A = \frac{n_A}{n_A + n_B} p_A^0 = N_A p_A^0 \quad [4]$$

where  $p_A$  is the partial pressure of the component  $A$ ,  $p_A^0$  is the vapor pressure of the pure substance and  $n_A/(n_A + n_B)$ , or  $N_A$ , is the mole fraction of the component  $A$ . Likewise in an ideal solution of two components the vapor pressure of the other component would be given by the expression

$$p_B = N_B p_B^0$$

*Example 2.* The vapor pressure of pure benzene at  $20^\circ$  is 74.7 mm. What is the partial pressure of benzene above a solution of benzene and toluene having a mole fraction of 0.9 benzene? These two liquids form a solution which is nearly ideal.  $0.9 \times 74.7 = 67.2$  mm.

If there are more components present in an ideal solution, each will have a partial pressure equal to its vapor pressure in the pure state multiplied by its mole fraction in the solution.

In an ideal solution the behavior of each substance is unaffected by the presence of the other. For example, the attraction between the  $A$  molecules,  $A-A$ , is just the same after the molecules have been dispersed through the solution, and the attraction between the  $B$  molecules,  $B-B$ , is just the same as in pure  $B$ . Methanol, for example, forms an ideal solution with ethanol, and a given molecule behaves just the same as it did before mixing. The fraction of molecules getting to the surface where they can pass off into the vapor is equal to the mole fraction in the solution. Ideal solutions are rare. They are more likely to be found when both components are similar chemically.

In a non-ideal solution there may be attraction between  $A$  and  $B$  molecules,  $A-B$ , greater than the  $A-A$  attraction or the  $B-B$  attraction. This may result in the lessening of the partial vapor pressures of  $A$  and  $B$ . Again, the presence of  $B$  molecules may cause the  $A-A$  attraction to decrease and thus increase the partial vapor pressure of  $A$ ; and the presence of  $A$  may decrease the force of attraction between  $B$  and  $B$  so that the escaping tendency or vapor pressure of  $B$  is increased. These changes in the  $A-A$  and the  $B-B$  attractions may be manifested as heat effects or volume changes or abnormalities in



viscosity, surface tension, and other properties, but the vapor pressure change is usually considered the most significant.

The exact interactions of  $A-A$ ,  $B-B$ , and  $A-B$  have not been worked out quantitatively yet, but the general principles of electrostatic attractions between ions, dipoles, and induced dipoles discussed on pages 11 and 648 seem to be well established.

In Tables I, II, and III, three different types of solutions are illustrated.\* The total pressures are obtained by adding together the two partial pressures. The calculated partial pressures  $P_{\text{calc}}$  are obtained by multiplying the vapor pressure of the pure liquid by its mole fraction in the solution. The data are shown graphically in Fig. 50, 51, and 52. The broken lines give the values of  $P_{\text{calc}}$ .

One of the common type of interactions leading to non-ideal solutions is that in which a hydrogen bond can be formed, making the  $A-B$  attraction greater than the  $A-A$  or the  $B-B$  attraction. Thus when a carboxylic acid such as acetic or formic acid or a ketone such as acetone, containing a double bond oxygen or other proton acceptor, is mixed with a substance which can be a proton donor, such as  $\text{CHCl}_3$  or a group such as  $\text{NH}$  which holds its hydrogen loosely, the solution will probably be non-ideal and the partial vapor pressures of the two components will probably be less than the calculated values. Thus  $\text{CCl}_4$  and acetic acid should give a more nearly ideal solution than chloroform and acetic acid.

The benzene-ethylene chloride solution is an ideal solution in which the experimentally determined total and partial pressures agree exactly with the calculated partial and total pressures.

In the acetone-chloroform solution the observed values are considerably less than the calculated values. The acetone molecules are held back in solution by the chloroform molecules more than by other acetone molecules; and the chloroform molecules are held back more by the acetone molecules. This mutual attraction is to be expected in view of the fact that an actual chemical compound  $(\text{CH}_3)_2\text{CO} \cdot \text{CHCl}_3$  is formed, which indeed can be isolated. With other substances the mutual attraction caused, at least in part, by an attraction between dipoles or between dipoles and induced dipoles, is sufficient to produce non-ideal solutions and yet insufficient to give a recognizable chemical compound between the two.

The acetone-carbon disulfide solution is typical of those solutions which give abnormally large vapor pressures—the molecules require less energy to get into the gas phase than when surrounded by molecules of their own kind.

\* Zawidzki, *Z. physik. Chem.*, **35**, 129 (1900).

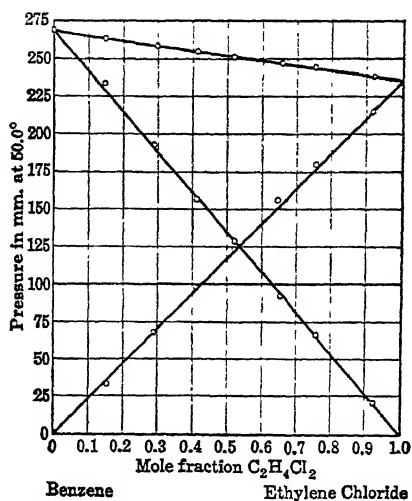


FIG. 50

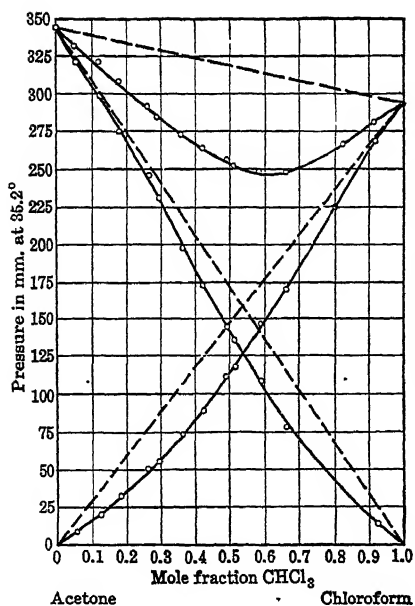


FIG. 51

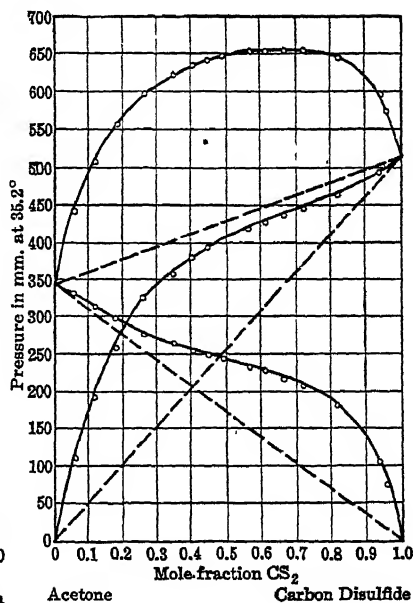


FIG. 52

TABLE I  
BENZENE-ETHYLENE CHLORIDE

Mole Fraction $C_2H_4Cl_2$	Benzene		Ethylene Chloride		Total	
	$P_{obs}$	$P_{calc.}$	$P_{obs}$	$P_{calc.}$	$P_{obs}$	$P_{calc.}$
0	268	268	0	0	268	268
0.2	215	215	47	47	262	262
0.4	161	161	94	94	255	255
0.6	108	108	141	141	249	249
0.8	54	54	188	188	242	242
1.00	0	0	236	236	236	236

TABLE II  
ACETONE-CHLOROFORM

Mole Fraction Chloroform	Chloroform		Acetone		Total	
	$P_{obs.}$	$P_{calc.}$	$P_{obs.}$	$P_{calc.}$	$P_{obs}$	$P_{calc.}$
0	0	0	344	344	344	344
0.2	34	59	270	275	304	334
0.4	82	117	183	207	265	324
0.6	148	177	102	137	250	314
0.8	225	236	42	67	267	303
1.00	293	293	0	0	293	293

TABLE III  
ACETONE-CARBON DISULFIDE

Mole Fraction $CS_2$	Acetone		Carbon Disulfide		Total	
	$P_{obs.}$	$P_{calc.}$	$P_{obs.}$	$P_{calc.}$	$P_{obs.}$	$P_{calc.}$
0	344	344	0	0	344	344
0.2	290	275	280	102	570	377
0.4	255	204	378	206	633	410
0.6	230	138	425	306	655	444
0.8	190	67	460	410	650	477
1.00	0	0	512	512	512	512

**Raoult's Law and Henry's Law.** The simple relation expressed in equation (4) was discovered empirically in 1884 by Raoult for a solvent containing small quantities of solute. The solute is so dilute that the solvent is but slightly affected. Raoult's law may be expressed as follows:

$$p_{\text{solvent}} = p_{\text{solvent}}^0 N_{\text{solvent}} \quad [5]$$

According to this law the partial vapor pressure of the solvent is equal to the vapor pressure of the pure solvent multiplied by the mole fraction of the solvent in the solution.

Henry's law applies to the solute.

$$p_{\text{solute}} = K N_{\text{solute}} \quad [6]$$

The partial vapor pressure of the solute is proportional to the mole fraction of the solute. This equation is distinctly different from Raoult's law in that the proportionality constant  $K$  is not the vapor pressure of the pure solute but a constant which must be evaluated experimentally for each solution. The difference lies in the fact that the solute is diluted to such an extent that its properties may be quite different from those of the solute in its pure state. Raoult's law applies to the solvent in solutions so dilute that the properties of the solvent are not greatly different from those of the pure solvent. In an ideal solution Henry's law, as well as Raoult's, is an exact law and equation (6) becomes identical with equation (4). Moreover the proportionality constant  $K$  becomes identical with the vapor pressure of the pure solute.

In non-ideal solutions the value of  $K$  in Henry's law is determined by measuring the vapor pressure at known mole fractions. Then

$$K = \frac{p_{\text{solute}}}{N_{\text{solute}}} \quad [7]$$

and the same values of  $K$  should be obtained from data at different mole fractions. In practice the law is not exact, and the properties of the dissolved solute, including its escaping tendency, change as the concentration changes.\*

**Solutions of Gases in Liquids.** When a dissolved substance evaporates into a closed space the concentration of molecules increases, and the rate at which the vapor molecules return to the solution increases until a dynamic equilibrium is attained. The partial pressure in the gas space under these conditions is the partial vapor pressure of the solute in solution. The solute can be a permanent gas just as well as a liquid or a solid, and it then seems more natural to look at the phenomenon as a solubility of gas in the solvent rather than as the solute escaping to give a definite vapor pressure. However, equation (6) is still applicable; in fact it was in studying the solubility of gases in liquids that Henry discovered this relationship.

\* If the "constant"  $K$  changes, the most significant value to take is the one obtained by plotting a few values of  $p/N$  against  $N$  for the solute and extrapolating it to infinite dilution as shown on page 525.

The solubilities of a few gases are given in Table IV in terms of Henry's constant  $K$  in which the concentration of the gas phase, expressed in millimeters of pressure, is divided by the concentration of the gas in solution expressed in mole fraction.

TABLE IV  
SOLUBILITY OF GASES AT 25°

$$K = \frac{p_A}{N_A} = \frac{\text{pressure of gas } A \text{ in millimeters}}{\text{mole fraction gas } A \text{ in solution}}$$

Gas	Solvent	
	Water	Benzene
H <sub>2</sub>	5 34 × 10 <sup>7</sup>	2.75 × 10 <sup>6</sup>
N <sub>2</sub>	6 51 × 10 <sup>7</sup>	1.79 × 10 <sup>6</sup>
O <sub>2</sub>	3 30 × 10 <sup>7</sup>	
CO	4 34 × 10 <sup>7</sup>	1.22 × 10 <sup>6</sup>
CO <sub>2</sub>	1.25 × 10 <sup>6</sup>	8.57 × 10 <sup>4</sup>
CH <sub>4</sub>	31.4 × 10 <sup>6</sup>	4.27 × 10 <sup>6</sup>
C <sub>2</sub> H <sub>2</sub>	1 01 × 10 <sup>6</sup>	
C <sub>2</sub> H <sub>4</sub>	8 67 × 10 <sup>6</sup>	
C <sub>2</sub> H <sub>6</sub>	23 0 × 10 <sup>6</sup>	

Sometimes the solubilities are expressed in terms of Bunsen coefficients, which give the number of liters of gas reduced to 0° and 760 mm. pressure which will dissolve in one liter of the solvent under a pressure of 760 mm. at a specified temperature.

*Example 3.* Express the solubility of carbon dioxide in water at 1 atm. pressure and 25° in terms of moles  $n$  per liter, assuming that the liter of solution contains practically 1000 g. of water

$$K = 1.25 \times 10^6 = \frac{760}{n_{\text{CO}_2}} \left( n_{\text{CO}_2} + \frac{1000}{18.02} \right)$$

The number of moles of carbon dioxide  $n_{\text{CO}_2}$  may be considered negligibly small in comparison with the number of moles of water, 1000/18.02. Then

$$n_{\text{CO}_2} = \frac{760 \times 55.55}{1.25 \times 10^6} = 3.38 \times 10^{-2} \text{ moles per liter}$$

The Bunsen solubility coefficient for carbon dioxide may be calculated from this value, giving  $\frac{3.38 \times 10^{-2} \times 22.41}{1} = 0.757$ .

As a first approximation, the volume of gas which dissolves is independent of the pressure above the solution because the number of

moles of dissolved gas changes directly as the pressure, and the volume of the gas above the solution changes inversely as the pressure.

Henry's law, like most of the laws of solutions, is not exact except in very dilute solutions. Up to a pressure of 1 atm. it holds within 1 to 3 per cent with many gases.

Dalton showed that the solubility of the individual gases in a mixture of gases is directly proportional to their partial pressures, the solubility of each gas being nearly independent of the presence of the others. The solubility of oxygen in water is nearly twice as great as that of nitrogen, and since the solubility of one gas is unaffected by the presence of the other, the dissolved air is considerably richer in oxygen than the air above water.

Theoretical explanations of the solubility of unreactive gases in liquids have been incomplete. A few empirical facts regarding the subject will be helpful in eventually formulating a satisfactory theory.

(a) The order of increasing solubility of gases in a liquid usually remains the same in different liquids.

(b) The increase in volume caused by the solution of a mole of the gas in a solvent is nearly equal to the corresponding value of  $b$  in the equation of van der Waals.

(c) The solubility of a gas in liquids is usually decreased by an increase in temperature. There are numerous exceptions, however, especially with the solvents liquid ammonia, molten silver, and many organic liquids.

(d) The solubility of gases in water is usually decreased by the addition of other solutes, particularly electrolytes. The extent of this "salting out" varies considerably with different salts, but with a given salt the relative decrease in solubility is the same for different gases. For example, if a certain salt reduces the solubility of oxygen in water to 80 per cent of its value, it will also reduce the solubility of nitrogen in water to about 80 per cent of its value.

The solubility of the unreactive gases is probably caused by an attractive force between the solute molecules and the solvent molecules due to dipole-induced dipoles (page 649), more generally referred to as van der Waals forces. Consider the solubility of helium in water. Helium molecules can certainly have no unbalanced electrical forces, and the attractive force due to electrical dipoles which they induce in each other is so weak that it is overcome by the slight thermal agitation which exists at 4° K., the boiling point of helium. Water molecules, on the other hand, have a considerable dipole moment, and, although the molecule as a whole is neutral, the charged parts induce an opposite charge in a neighboring molecule and a force of attraction

is set up between the two. Many molecules can thus be crowded into a liter of water even though the vessel appears to be filled with water molecules. A similar example is found in the solubility of butane in water. The supposedly inert butane molecule has been found to form a solid hydrate with water. This unexpected phenomenon was a technical problem in the passage of butane gas through pipes in cool weather.

The salting-out effect can be explained on the hypothesis that it is caused by the hydration of the salt. A portion of the water combines with the salt, and the water which is thus removed from the role of solvent is no longer free to absorb gas. More specifically one can consider that the water molecules with their electrical dipoles are partially oriented with respect to the ions or dipoles of the dissolved salt and are less free to induce dipoles in the molecules of gas.\*

It is common observation that a glass of cold water, when warmed to room temperature, shows the presence of many small air bubbles. The rate of escape of the molecules of dissolved gas from the liquid is increased more by an increase in temperature than is the rate at which molecules of the gas phase strike the surface and dissolve in the liquid leading to a decreased solubility. From an energy standpoint, the forces of attraction which cause the gas molecules to crowd into the liquid are partially offset by the increased kinetic energy at the higher temperatures.

These discussions have been concerned with relatively inert gases, but the conclusions regarding salting out and temperature effects apply also to chemically active gases such as hydrochloric acid or ammonia which ionize in aqueous solutions.

**Vapor Composition of Binary Systems.** If an ideal solution could be found composed of two liquids with identically the same vapor pressures the composition of the vapor would be the same as that of the liquid. But if one of the components has a higher vapor pressure than the other it will be present in excess in the vapor even when there are the same number of molecules of each in the liquid, i.e., at mole fraction such that  $N_A = N_B = 0.5$ . In fact, at all mole fractions the vapor will be richer than the liquid in the more volatile component. The same general considerations apply to solutions which are not ideal, but in these solutions the partial pressures cannot be calculated with exactness from the mole fractions.

In **Fig. 53** the total vapor pressure of a solution is plotted against the mole fraction of the component which has the higher vapor pres-

\* The influence of salting out on the dipole of a second substance has been measured by Williams and Albright, *Trans. Faraday Soc.*, **33**, 247 (1937).

sure. There must be two curves, one for the liquid and one for the vapor composition. The temperature is constant. More often the boiling temperatures (the temperature at which the total pressure becomes equal to the external pressure) are plotted against the mole fraction as shown in Fig. 54.

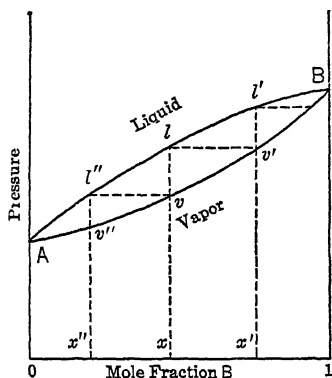


FIG. 53

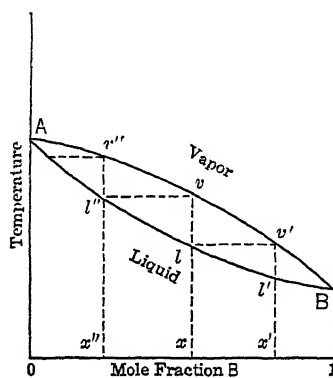


FIG. 54

The curve  $Al''wB$  in Fig. 53 gives the total vapor pressure exerted by a liquid of the composition given on the  $x$  axis. The curve  $Av''vv'B$  gives the pressure at which vapors of a specified composition first show a tendency to form a liquid phase. When a horizontal line such as  $lw'$  is drawn, the intersections with the two curves give the composition of the liquid phase and of the vapor phase under equilibrium conditions.

Since the vapor is relatively richer in the more volatile component, it follows that the curve representing vapor composition must always lie closer to the component which has the higher vapor pressure. For example, in Fig. 53, since  $B$  is seen to have a higher vapor pressure than  $A$  the vapor curve must lie nearer to the side corresponding to pure  $B$  than does the curve which gives the compositions of the liquid. If  $x$  denotes the mole fraction of  $B$  in the liquid phase,  $x'$  is the equilibrium concentration of  $B$  in the vapor phase; or, if  $x$  denotes the concentration of  $B$  in the vapor phase,  $x''$  is the equilibrium concentration in the liquid phase.

Similar considerations apply to the temperature-composition curves of Fig. 54.

**Maximum and Minimum Boiling Points.** In some cases, the departure from ideal behavior is so great that the curves exhibit actual maxima as shown in Fig. 55.

The mixture of hydrochloric acid and water has been studied exten-



TABLE V

BINARY MIXTURES HAVING MAXIMUM BOILING POINTS

Components	Boiling Point (Pressure = 760 mm.)	Composition of Mixture at Boiling Point
Water + $\text{HNO}_3$	120.5°	68% $\text{HNO}_3$
Water + $\text{HCl}$	108.6°	20.2% $\text{HCl}$
Water + $\text{HBr}$	126	47.5% $\text{HBr}$
Water + $\text{HI}$	127	57.0% $\text{HI}$
Water + $\text{HF}$	120	37.0% $\text{HF}$
Water + $\text{H}\cdot\text{COOH}$	107.1	77.9% $\text{H}\cdot\text{COOH}$
$\text{CHCl}_3$ + $\text{CH}_3\text{COCH}_3$	64.7	80.0% $\text{CHCl}_3$

sively, and the composition of the constant-boiling mixture is so reproducible that it is used as a standard in quantitative analysis. If any solution of hydrochloric acid is boiled for a sufficient time under a pressure of 760 mm. the temperature will gradually rise to 108.6° and remain stationary, and the mixture boiling at this constant temperature

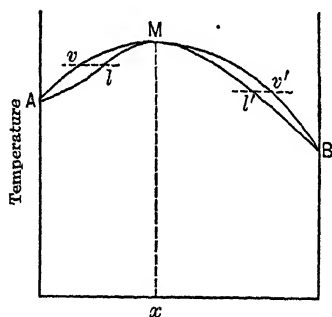


FIG. 55

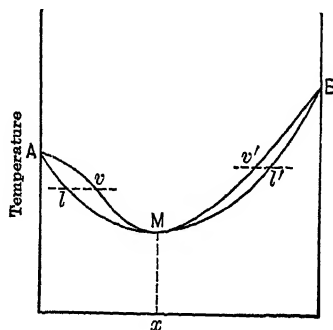


FIG. 56

will contain 20.2 per cent hydrochloric acid by weight. From solutions containing less than 20.2 per cent it is possible by continued fractional distillation to recover pure water in the distillate, but it is not possible to recover pure hydrogen chloride. It may be recovered, however, by fractional distillation of a mixture containing more than 20.2 per cent.

A large number of pairs of liquids are also known whose boiling-point curves pass through a minimum as shown in Fig. 56. Ethanol boiling at 78.3° and water boiling at 100° give a curve of this type, and a minimum boiling point of 78.13° occurs with a solution which is 95.57 per cent alcohol by weight. Any mixture containing less than 95.57 per cent of ethanol can be separated completely by fractional

distillation into pure water and 95.57 per cent ethyl alcohol. Propyl alcohol gives a more pronounced minimum.

Maxima and minima are not confined to vapor-pressure and boiling-point curves, but they are sometimes found when freezing points, densities, viscosities, specific heats, and other properties are plotted against composition. *They are not found in ideal solutions.* Whenever a maximum exists, there must be at least two opposing factors, one tending to increase the magnitude of the property and the other tending to decrease it as the concentration is changed.

In respect to hydrochloric acid and water the minimum in the vapor-pressure curve, or maximum in the boiling-point curve, is due to the ionization of hydrochloric acid. Water and pure hydrochloric acid have high vapor pressures, but the hydrogen ions and chloride ions cannot escape from the solution. It will be shown in the next chapter that they lower the vapor pressure of the water. In small amounts, hydrochloric acid added to water lowers the vapor pressure through its ions; but in large amounts, it increases the vapor pressure by adding to the solution the more volatile hydrochloric acid molecules, a fact which can be realized from the sharp odor of hydrochloric acid in the concentrated solutions.

It was thought for a long time that maxima of this type correspond to definite chemical compounds, and such is actually true in freezing-point curves which will be studied later. The composition of 20.2 per cent HCl in the constant-boiling mixture corresponds very closely to the formula  $\text{HCl} \cdot 8\text{H}_2\text{O}$ , but the relation is accidental. It has been proved that such mixtures are not definite chemical compounds since the composition of the distillate changes when the distillation is carried out under different pressures. Usually these maxima do not come at compositions corresponding to any chemical formula, and if maxima in two different properties occur in the same mixture, they often occur at different compositions.

Chemical combination between the two liquids or attraction due to the existence of dipoles or induced dipoles in the molecule is, nevertheless, a factor in many solutions. The tendency for two liquids to attract each other in a loose compound through the formation of a hydrogen bond (page 647) is responsible for the formation of several binary systems with a minimum vapor and maximum boiling point, particularly if the vapor pressures are fairly close together. Supporting this view, Ewell and Welch\* have shown that most of the ketones form with alkyl halides boiling-point curves with maxima if the boiling points are close together.

\* Ewell and Welch, *J. Am. Chem. Soc.*, **63**, 2475 (1941).

**Distillation of Binary Systems.** When binary systems are distilled under constant pressure three types of boiling-point curves can be distinguished. In the first type, shown in Fig. 54, the boiling points of all the mixtures are intermediate between those of the two components. All mixtures of the second type, shown in Fig. 55, exhibit a maximum in their boiling-point curves, whereas mixtures of the third type, shown in Fig. 56, exhibit a minimum.

The lower-boiling-point component, i.e., the component with the higher vapor pressure, is present in relatively greater amount in the vapor phase, and, accordingly, the upper curve corresponds to the vapor phase in all these diagrams in which boiling temperatures are plotted along the  $y$  axis.

Any binary mixture of the first type can be more or less completely separated into its components by the process of *fractional distillation*. In Fig. 54, if  $x''$  represents the composition of a large quantity of liquid at  $l''$ ,  $x$  represents the composition of the first vapor,  $v$ , to be distilled and if this vapor is condensed by cooling to  $l$  and again distilled, the vapor,  $v'$ , will now have the composition represented by  $x'$ . In other words, by the process of fractional distillation the concentration of the more volatile component,  $B$ , has been increased in the distillate and correspondingly decreased in the residue. By continuing the process of successive condensation and distillation it is possible to obtain pure  $B$  in the distillate and pure  $A$  in the residue. In practice each successive distillation involves an appreciable change in concentration and the average concentration must be considered.

Binary mixtures of the second type exhibit a maximum in their boiling-point curves, as shown at  $M$  in Fig. 55. On distilling a mixture the initial composition of which corresponds to  $l$ , the liquid phase becomes relatively richer in the component  $B$ , and the boiling point continues to rise until, ultimately, the liquid phase acquires the composition corresponding to  $M$ . The liquid and vapor then have the same composition, and distillation proceeds without further change in composition provided the pressure remains constant. Such a solution which distills without change in composition or temperature is called an *azeotropic solution*.

Similarly, if a mixture having an initial composition which corresponds to  $l'$  is distilled, the liquid phase becomes relatively richer in the component  $A$ , and finally acquires the composition of the mixture  $M$ , having the maximum boiling point.

The third type of boiling-point curve has a minimum, as shown in Fig. 56. Any mixture whose composition lies between that of  $A$  and  $M$  may be separated more or less completely into pure  $A$  and the mix-

ture  $M$  by fractional distillation. Pure  $A$  is then left in the residue, and the mixture  $M$  having the composition  $x$  is obtained as the distillate. In like manner, mixtures whose composition lies between that of  $B$  and  $M$  can also be separated by fractional distillation into pure  $B$  and the mixture  $M$ . Pure  $B$ , however, cannot be obtained on distilling a mixture whose composition lies between that of  $A$  and  $M$ .

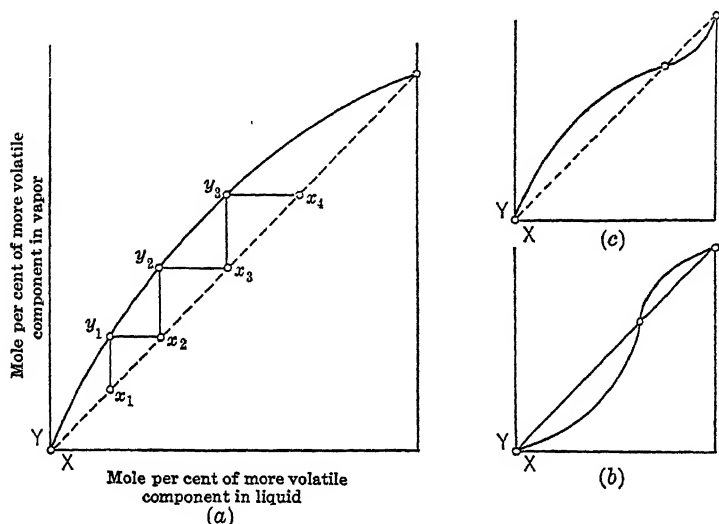


FIG. 57

**Fractional Distillation.** When a mixture of two liquids vaporizes, that component which has the higher partial vapor pressure tends to concentrate in the vapor, thus producing a difference in composition between the liquid and the vapor which is in equilibrium with it. The situation is represented in Fig. 57a for a simple binary mixture in which there is no maximum nor minimum in the boiling curve. The data of the figure are only for one pressure; data at other pressures give similar curves. The dotted line which makes an angle of  $45^\circ$  with the  $x$  axis is such that any point on it has the same value along the  $x$  and  $y$  axes; in other words, the composition of vapor and liquid along this hypothetical line is the same. The full line along  $y_1$  and  $y_3$  gives the composition of vapor plotted along the  $y$  axis corresponding to any composition of liquid plotted along the  $x$  axis. If the mixture has a minimum vapor pressure as in Fig. 51 the curve intersects the  $45^\circ$  line with a maximum slope as shown in Fig. 57b. If the mixture has a maximum, as in Fig. 52, it intersects with a minimum slope as shown in Fig. 57c. In Fig. 57a, there are two points where the composition

of vapor and liquid is the same, namely, pure *A* and pure *B*. In Figs. 57*b* and *c* there is a third point where they are the same, namely, at the maximum or minimum boiling point.

The process of fractional distillation may be illustrated by reference

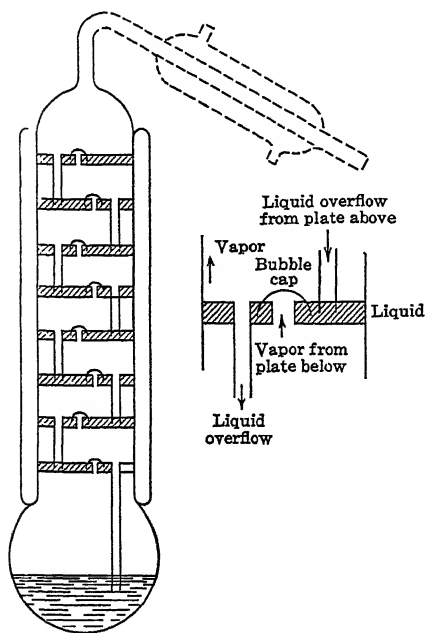


FIG. 58

to Fig. 57*a*. Starting with a large amount of liquid of composition  $x_1$  and evaporating a small portion, the vapor will be found to have the composition  $y_1$ . If all this vapor is condensed, its composition will remain unchanged. Calling the composition of the condensed liquid  $x_2$  it follows that  $x_2 = y_1$ . When a very small portion of this liquid of composition  $x_2$  is evaporated, the vapor will have the composition  $y_2$ . If this process of evaporation and condensation is continued, it is possible to obtain a very small amount of the more volatile component in a practically pure state at *B*.

A series of successive vaporization and condensations may be carried out in a fractionat-

ing column. The simplest form to visualize is the tower of bubble caps diagrammed in Fig. 58.

At total reflux fresh liquid of constant composition corresponding to composition  $x_1$  of Fig. 57 is fed in at the bottom and vapor from it bubbles out through the liquid in the first or lowest trough. The composition of this liquid corresponds to  $y_1$  or  $x_2$ . The vapor from the first layer of condensed liquid now corresponds to  $y_2$  and it passes up through the second bubble cap where it is condensed to give the second layer of liquid having composition  $x_3$  which is equal to that of  $y_2$ . The overflow is returned to the first layer and eventually down to the residue. The process is continued through a whole series of liquid layers. Each layer is called a plate. The distillate at the top is greatly enriched in the more volatile component, some enrichment taking place at each condensation and evaporation, i.e., at each plate.

The column is well insulated or it is surrounded by a controlled

heating jacket so that there will not be general condensation on the walls. The whole system reaches a state of equilibrium in which the composition of liquid on each plate remains unchanged. In actual practice for continuous distillation the incoming liquid is fed into the tower near the middle.

In the laboratory, distillations are usually carried out in batches, and the liquid in the bottom is gradually reduced in volume as the vapor at the top is distilled out and recovered by condensation. The mathematical analysis under these conditions is more complicated but if the column is operated at nearly total reflux, so that very little of the vapor is distilled out, a state of equilibrium is reached which is practically the same as that described for the continuous flow operation.

The bubble cap towers are not often used because it is simpler to pack the tower with material which will provide efficient contact between liquid and vapor and will occupy only a small volume so that there is free space to permit a large through-put of vapor. Helices of glass, spirals of screen and various types of packing\* are used and it is convenient to know how efficient such a column is. The efficiency of a column is expressed in terms of the number of theoretical plates to which it is equivalent. A theoretical plate may be visualized as a layer in a 100 per cent efficient bubble cap tower, i.e., one in which the vapor leaving the plate is in complete equilibrium with the circulating liquid on the plate. The number of theoretical plates can be determined very simply by finding the composition of the exit vapors and that of the liquid in the distilling flask under conditions of total reflux, marking these two points on the 45° line of Fig. 57*a* and finding the number of horizontal-vertical steps which can be drawn between the two compositions. Thus, if the composition of the distillate is found to be  $x_4$  in the distillate and  $x_1$  in the residue there can be drawn three steps connecting the two. Since the distilling pot itself corresponds to one theoretical plate the column for which this figure applies has two theoretical plates.

A fractionating column operating at total reflux obviously would not be very practical for separating liquids, but the higher the reflux ratio, i.e., the greater the ratio of liquid returned to the distilling flask to the vapor distilled out, the greater is the efficiency of separation. An ordinary distilling flask and unpacked column may be equivalent to one or two theoretical plates, but when well packed, it

\* Daniels, Mathews, and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1941. Page 338.

Morton, "Laboratory Techniques in Organic Chemistry," McGraw-Hill Book Co., New York. Chapter IV.

is possible to have the equivalent of a theoretical plate every inch or so. Fractionating columns of 10 to 20 theoretical plates operating at a reflux ratio of 10 to 1 effectively separate liquids which have boiling points so close together that they cannot be separated in a simple distillation flask. Marked improvements have been made recently in laboratory distillations and purifications, as well as in industrial distillations. The demands of the petroleum industry have given an impetus to the development of the theory and practice of fractional distillation.

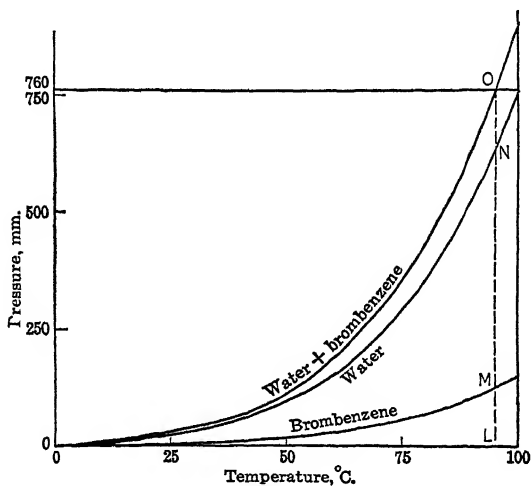


FIG. 59

**Immiscible Liquids.** The vapor-pressure relations of two immiscible liquids are shown in Fig. 59. Each exerts its own vapor pressure independently of the other. The total vapor pressure is obviously the sum of the vapor pressures of the two liquids if neither liquid dissolves in the other, and the vapor pressure and composition of the vapor are constant at constant temperature, independent of the composition of the liquid.

In the example shown the total vapor pressure reaches atmospheric pressure  $LO$  at  $95^\circ$ , and both liquids distil together at this temperature. When either one of the liquids has completely distilled away at this temperature the vapor pressure drops to that of the remaining liquid,  $LM$  or  $LN$ .

Since the pressure of a gas is proportional to the number of molecules in a given space, we may express the relation between vapor

pressure and composition by the equation:

$$\frac{p_A}{p_B} = \frac{n_A}{n_B} \quad [8]$$

where  $p_A$  and  $p_B$  are the vapor pressures, and  $n_A$  and  $n_B$  are the number of moles of  $A$  and  $B$ . If  $w_A$  and  $w_B$  denote the weights in grams of  $A$  and  $B$  in a known weight of vapor, and if  $M_A$  and  $M_B$  are their respective molecular weights, distilling off and condensing in a given time interval

$$n_A = \frac{w_A}{M_A} \quad \text{and} \quad n_B = \frac{w_B}{M_B}$$

On substituting these values in equation (8):

$$\frac{p_A}{p_B} \cdot \frac{M_A}{M_B} = \frac{w_A}{w_B} \quad [9]$$

*Steam distillation* is a common laboratory and engineering operation which makes use of this relation. It is a more convenient operation than vacuum distillation and accomplishes the same purpose, namely, rapid evaporation and condensation at a comparatively low temperature. This is an asset particularly when the material is likely to decompose if heated to its normal boiling point.

If an organic substance is not decomposed by steam, it is possible to effect a purification by steam distillation, even though the vapor pressure is relatively low. It is the low molecular weight and the cheapness of water which render it so suitable for distillations of this kind.

*Example 4.* How many grams of water would be required to steam-distil a kilogram of bromobenzene? The vapor pressure of bromobenzene is 125 mm. at 95° and that of water is 635 mm.

$$\frac{p_{\text{H}_2\text{O}}}{p_{\text{C}_6\text{H}_5\text{Br}}} \times \frac{M_{\text{H}_2\text{O}}}{M_{\text{C}_6\text{H}_5\text{Br}}} = \frac{635}{125} \times \frac{18}{157} = \frac{w_{\text{H}_2\text{O}}}{1000} \cdot \quad w_{\text{H}_2\text{O}} = 583 \text{ g.}$$

The behavior of partially miscible liquids is similar to completely miscible liquids as long as there is only one liquid layer, showing that the two liquids dissolve completely in each other. When the mutual solubility is exceeded and two layers are formed, the vapor-pressure relations resemble those of the immiscible liquids.

In general, the boiling-point curves for mixtures of two partially miscible liquids are like those shown in **Fig. 60**. Mixtures in which the mole fraction of  $B$  lies between 0 and  $x$ , and also between  $x'$  and



1 consist of a single homogeneous liquid phase. On the other hand, all mixtures whose compositions are included between  $x$  and  $x'$  consist of two homogeneous liquid phases. If a mixture whose composition corresponds to  $l$  is evaporated, the initial portions of vapor have the composition corresponding to  $v$ . As evaporation proceeds, the temperature rises and the composition of the liquid phase alters, until eventually nothing but pure  $A$  remains in the distilling flask. In like manner, if a homogeneous mixture where composition corresponds to  $l'$  is evaporated, the boiling point will gradually rise, until that of the pure component  $B$  is reached. On the other hand, when any mixture with a composition lying between  $x$  and  $x'$  is distilled,

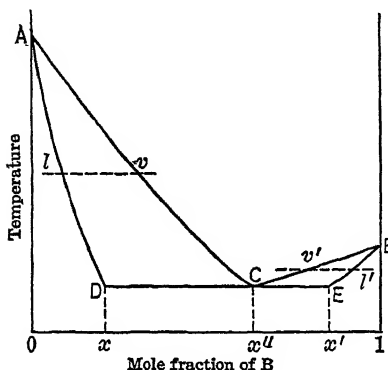


FIG. 60

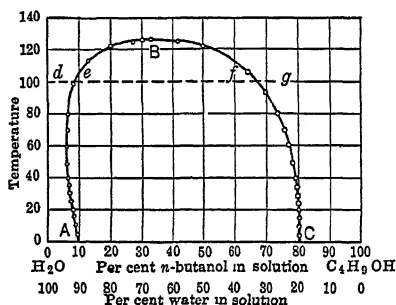


FIG. 61

the boiling point remains constant as long as the two liquid phases are present. The composition of the two phases is represented by  $x$  and  $x'$  and the composition of the vapor from each phase is represented by  $x''$ , this being the composition corresponding to the intersection of the vapor curves,  $AC$  and  $BC$ . If the process of distillation is continued for a sufficient time, one of the two liquid phases disappears. If the original two-phase liquid mixture is richer in component  $A$  than the composition  $x''$ , the phase represented by  $x'$  will disappear, and the boiling point will increase along  $DA$ . Similarly, if the original mixture is richer in component  $B$  than the composition  $x''$ , the phase represented by  $x$  will disappear ultimately, and the boiling point will increase along  $EB$ . Numerous mixtures of this kind are known; for example water (b. p.  $100^\circ$ ) and *iso*-butanol (b. p.  $108.4^\circ$ ), which form a two-phase mixture boiling at  $88.5^\circ$  under a pressure of 760 mm.

Sometimes two liquids are completely soluble in all proportions at

certain temperatures and only partially soluble at other temperatures. Water and *n*-butanol exhibit such behavior as shown in Fig. 61. In all regions inside the curve *ABC* there are two liquid layers while outside there is but one. Temperature is plotted vertically along the *y* axis and percentage composition of the solution horizontally along the *x* axis. Starting with a small amount of butanol and adding it in increasing quantities to a large volume of water, a concentration eventually will be reached at which the solution separates into two layers. This concentration at 0° is represented by the point *A*. On raising the temperature, the solubility of butanol in water increases, as shown by the curve *AB*. In like manner, starting with pure butanol and adding increasing amounts of water at 0°, separation into two layers occurs at a concentration represented by the point *C*. As the temperature is raised, the solubility of water in butanol increases, as shown by the curve *CB*. When the temperature is raised above 126° corresponding to the height of the point *B*, butanol and water become soluble in all proportions.

If one starts with a solution at a temperature and composition represented by the point *d*, the addition of increasing amounts of butanol at constant temperature is represented by the dotted line *defg*. When the point *e* is reached, the solution separates into two layers. As more butanol is added the quantity of the butanol layer saturated with water, increases, but the compositions of the two layers remain constant. At *f* the solution again becomes homogeneous, and the addition of more butanol increases the concentration of butanol in the solution, as for example at *g*. A more detailed discussion of systems of this general type will be given in Chapter XIII.

The mutual solubilities of some pairs of partially miscible liquids were found by Alexejeff to diminish with increasing temperature. Thus, a mixture of ether and water, which is perfectly homogeneous at ordinary temperatures, becomes turbid on warming. With some mixtures, as nicotine and water, it is possible to obtain both a maximum and a minimum temperature beyond which only one homogeneous phase is obtained. At intermediate temperatures and within definite limits of concentrations two separate liquid phases are formed.

**Heat of Solution.** The heat effect which accompanies the dissolving of a mole of solute is known as the molal heat of solution. It changes with the concentration all the way from an infinitely dilute solution, i.e., pure solvent, to a saturated solution. The situation is illustrated in Fig. 62, where the heat absorbed when  $n_2$  moles of solute is dissolved in 1000 g. of pure solvent is plotted against the molality, i.e., the number of moles per 1000 g. of solvent. The addi-

tion of 1 mole of this solute to 1000 g. of water absorbs 1000 cal. of heat, and it might be expected that the addition of 2 moles to 1000 g. of solvent would absorb 2000 cal. However, the nature of the solvent is changed by the addition of the solute and the solute molecules can interact so that the heat effect usually is not directly proportional to the amount of solute added. In the hypothetical case illustrated, the

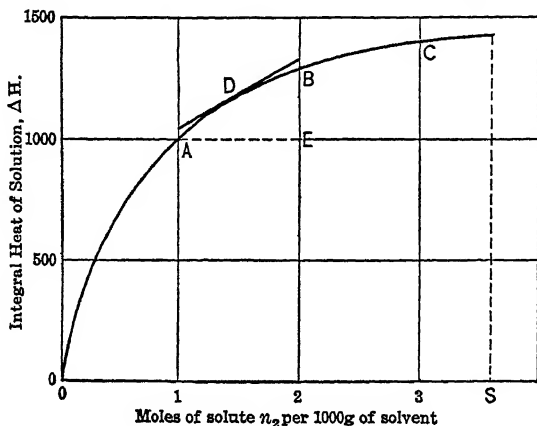


FIG. 62

addition of 2 moles of solute to 1000 g. of solvent absorbs 1300 cal., and the addition of 3 moles absorbs 1400 cal. However when the solution becomes saturated at  $S$ , the further addition of solute produces no further effect because no more can dissolve.

The *integral heat of solution* is defined as the heat absorbed when 1 mole of the solute is dissolved in a sufficient quantity of the solvent to give the specified concentration. In Fig. 62 the integral heats of solution at 1, 2, and 3 molal are, respectively,  $A$ ,  $B/2$  and  $C/3$ . It is possible also to calculate the heat absorbed when a given number of moles is added to a solution of specified concentration. Thus in Fig. 62 the addition of 1 mole of solute to a 1 molal solution containing 1000 g. of solvent absorbs  $B-E$  calories of heat.

The *differential heat of solution* is the heat of solution of a mole of solute in a quantity of solution so large that the addition of the one more mole of solute does not change appreciably the concentration of the solution. The notation of differential calculus is helpful. The differential heat of solution is defined as  $d(\Delta H)/dn_2$ , where  $\Delta H$  is the heat of solution of  $n_2$  moles of solute in 1000 g. of solvent. It is shown by the tangent at  $D$  for 1.5 molal solution. The average heat of solution obtained by dividing differences in  $\Delta H$  by the cor-

responding differences in  $n_2$  is not definite because it depends on the magnitude of the range of concentration changes which are taken. Before these methods of differential calculus were applied to solutions, confusion existed and different investigators reported different values for the same solutions.

The slope of the curve when  $n_2 = 0$  represents the heat absorbed when a mole of solute is dissolved in pure solvent, i.e., infinitely dilute solution. The slope of the curve when  $n_2 = s$  represents the heat absorbed when a mole of solute is dissolved in a large amount of nearly saturated solution.

The integral heats of solution are recorded for a number of solutes in Table VI. They give the values of  $\Delta H$  when 1 mole of the substance is dissolved in the number of moles of water specified — usually 200. When  $\Delta H$  is positive, heat is absorbed; when it is negative, heat is evolved.

TABLE VI  
INTEGRAL HEATS OF SOLUTION IN WATER AT 20°

Substance	Moles H <sub>2</sub> O	$\Delta H$ , kcal.	Substance	Moles H <sub>2</sub> O	$\Delta H$ , kcal.
HCl.....	200	-17.44	NaNO <sub>3</sub> .....	200	+ 5.01
HBr.....	200	-19.92	Na <sub>2</sub> SO <sub>4</sub> .....	400	- 5.50
HI.....	200	-19.24	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O...	400	+18.90
NH <sub>3</sub> .....	200	- 8.46	KCl... ..	200	+ 4.44
H <sub>2</sub> SO <sub>4</sub> .....	200	-17.75	KBr.....	200	+ 5.03
HNO <sub>3</sub> .....	200	- 7.48	KI.....	400	+ 5.12
NH <sub>4</sub> Cl.....	200	+ 3.90	KOH.....	250	-13.29
NH <sub>4</sub> NO <sub>3</sub> .....	200	+ 6.34	KNO <sub>3</sub> .....	200	+ 8.46
NaCl.....	200	+ 1.28	K <sub>2</sub> SO <sub>4</sub> .....	400	+ 6.55
CuCl <sub>2</sub> .....	600	-11.11	CuSO <sub>4</sub> .....	800	-15.89
CuCl <sub>2</sub> ·2H <sub>2</sub> O....	200	- 3.70	CuSO <sub>4</sub> ·5H <sub>2</sub> O....	800	+ 2.85
NaOH. ....	200	- 9.94			

Usually heat is absorbed when a crystalline salt dissolves, because in the solution process the atoms or ions are torn apart from each other in the crystal lattice. If this process is not offset by other processes it might be expected that as much heat would be absorbed as is absorbed in the fusion and vaporization of the crystal into the gas phase. Combination with the solvent can evolve heat which partially or wholly offsets this cooling effect. Particularly if the dissolved material gives ions, there is likely to be a strong electrical attraction between solute and the molecules of solvent which possess

a dipole moment. This attractive force leads to the formation of solvated ions and molecules, and to the evolution of heat.

The importance of this attraction of the solvent for the solute in the process of solution may be emphasized with the solution of sodium chloride. In the crystal lattice, positive sodium ions and negative chloride ions attract each other with great force. It can be calculated, by methods involving the ionization potential of sodium and chlorine and the heat of formation of sodium chloride, that 197,000 cal. per mole is necessary to break the combination to give separate ions. This energy is so great that nonpolar solvents like benzene or carbon tetrachloride will not dissolve sodium chloride; but a solvent like water, which has a large dielectric constant and a large dipole moment, combines with the ions and in so doing evolves a large amount of heat. In this way the large energy required for breaking up the crystal lattice is made available. With sodium chloride the heat of hydration just about offsets the heat of separation of the ions and there is very little heat effect. With some substances the combination with the solvent more than offsets the energy required to separate the units of the solute, and heat is actually evolved.

When a solution is diluted by the addition of more solvent there is a heat change corresponding to the difference in the integral heat of solution at the two concentrations. In Table VII are given the heats evolved when the mineral acids are diluted with definite amounts of water.

TABLE VII  
HEATS OF DILUTION OF ACIDS ( $\Delta H$  in kcal.)

Moles of H <sub>2</sub> O Added	To HNO <sub>3</sub> + H <sub>2</sub> O	To HCl + H <sub>2</sub> O	Moles of H <sub>2</sub> O Added	To H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O
1	-1.51	- 5 97	0.5	- 2.11
2	-2.44	- 7.98	1	- 3.30
4	-3.50	- 9.59	2	- 5.02
9	-4.04	-10 78	5	- 7.70
24	-4 23	-11.48	8	- 8 95
49	-4 18	-11 70	18	-10.43
99	-4 16	-11.90	48	-10 68
199	-4.16	-11 95	98	-10 90
399	-4.16	-12 00	198	-11.08
$\infty$	-4.16	-12.07	398	-11.40
			798	-11.82
			1598	-12.30
			$\infty$	-14.09

It is apparent that, as the dilution of these solutions is increased, the thermal effect produced by the addition of more solvent becomes less and less, and ultimately becomes zero.

## REFERENCES

- HILDEBRAND, "Solubility of Non-electrolytes," Reinhold Publishing Corp., New York, 1936.  
 ROBINSON and GILLILAND, "The Elements of Fractional Distillation," McGraw-Hill Book Co., New York, 1939.

## PROBLEMS

1. Zinc chloride ( $\text{ZnCl}_2$ ) weighing 350 g. is dissolved in 650 g. of water to give a solution with a total volume of 739.5 ml. at  $20^\circ$ . Calculate: (a) the molality of the solution, (b) the molar concentration of the solution, (c) the mole fraction of  $\text{ZnCl}_2$  in the solution, (d) the density of the solution, (e) the per cent by weight of zinc chloride. *Ans.* (a) 3.950. (b) 3.472. (c) 0.06644. (d) 1.3523. (e) 35.00.

2. Forty-eight grams of oxygen and 56 g. of nitrogen are contained in a 10-liter vessel at  $0^\circ$ . Calculate in atmospheres (a) the total pressure, (b) the partial pressure of each gas. *Ans.* (a) 7.85 atm. (b)  $p_{\text{O}_2} = 3.36$ ;  $p_{\text{N}_2} = 4.49$  atm.

3. At  $20^\circ$ , 1 volume of water absorbs 0.03405 volume of oxygen under atmospheric pressure, and 0.01696 volume of nitrogen under atmospheric pressure. When air (20.9 per cent oxygen and 79.1 per cent nitrogen by volume) is dissolved in water under atmospheric pressure, what is the percentage (by volume) of oxygen and of nitrogen in the dissolved gases?

*Ans.*  $\text{O}_2 = 34.65$ ;  $\text{N}_2 = 65.35$  per cent by volume.

4. Ethanol and methanol form a solution which is nearly ideal. The vapor pressure of ethanol is 44.5 mm. and that of methanol is 88.7 mm. at  $20^\circ$ . (a) Calculate the mole fraction of methanol and ethanol in a solution obtained by mixing 100 g. of each. (b) Calculate the partial pressures and the total vapor pressure of the solution. (c) Calculate the mole fraction of methanol in the vapor.

*Ans.* (a)  $N_{\text{CH}_3\text{OH}} = 0.590$ ;  $N_{\text{C}_2\text{H}_5\text{OH}} = 0.410$ .

(b)  $p_{\text{C}_2\text{H}_5\text{OH}} = 18.25$ ;  $p_{\text{CH}_3\text{OH}} = 52.32$ ;  $p_{\text{total}} = 70.6$ .

(c) 0.741.

5. The vapor pressures of benzene and carbon disulfide at  $20^\circ$ ,  $40^\circ$ , and  $80^\circ$  are as follows:

	$20^\circ$	$40^\circ$	$80^\circ$
$\text{C}_6\text{H}_6$ (mm.)	76.5	185	755
$\text{CS}_2$ (mm.)	297	617	2030

Calculate the total vapor pressure at each of the above temperatures for a mixture containing 1 mole of benzene in 1 mole of carbon disulfide. The observed values of the total pressure at the above temperatures are respectively as follows: 206 mm., 432 mm., and 1475 mm. Calculate the percentage deviation for each temperature. Is the solution more ideal in its behavior at the highest or lowest temperature?

*Ans.* More ideal at the highest temperature.

6. The vapor pressure of the immiscible liquid system diethylaniline-water is 760 mm. at 99.4°. The vapor pressure of water at that temperature is 744 mm. How many grams of steam are necessary to distil over 100 g. of diethylaniline?

*Ans.* 562 g.

7. When 1 mole of zinc nitrate is dissolved in a large excess of water, 84,720 joules of heat is evolved and when it is dissolved in just sufficient water to give 2.757 molal zinc nitrate, 82,480 joules of heat is evolved. What is the heat of dilution of this solution to infinite dilution? All the heats of reaction described in this problem are integral heats.

*Ans.* 2240 joules evolved.

8. A solution of  $\text{KNO}_3$  contains 192.6 g. of salt per liter of solution. The density of the solution is 1.1432. Calculate the concentration in terms of (a) molality, (b) molarity, (c) mole fraction, (d) weight per cent.

9. Exactly 1.100 g. of carbon dioxide was introduced into a 1-liter flask which contained some pure oxygen before being subjected to partial evacuation. The flask was warmed to 100° and the pressure found to be 608 mm. Hg. Considering oxygen and carbon dioxide to be the only gases present, calculate the weight of oxygen in the flask.

10. At 25° and 1 atm. pressure, the solubility of oxygen,  $\text{O}_2$ , in water is 0.001225 mole per liter. How many grams are dissolved in a lake which is 1 mile in diameter with an average depth of 20 ft., assuming complete equilibrium with the air?

11. The solubilities of carbon monoxide and nitrous oxide in water are 0.757 and 0.539 respectively, where solubilities are expressed in volume of gas under standard conditions per volume of solution. The solubility of carbon monoxide in 1.0 molal  $\text{Mg}(\text{NO}_3)_2$  is 0.559. Calculate the solubility of nitrous oxide in 1.0 molal  $\text{Mg}(\text{NO}_3)_2$ . The experimental value is 0.385.

12. Benzene and toluene form a solution which is nearly ideal. At 80° the vapor pressures of benzene and toluene are as follows: vapor pressure of benzene = 753 mm. Hg; vapor pressure of toluene = 290 mm. Hg. In a solution containing 0.5 mole fraction of benzene and 0.5 mole fraction of toluene, what is the composition of the vapor at 80°?

13. From the data given below construct a complete temperature-composition diagram for the system ethanol-ethyl acetate. The data apply to 760 mm. A solution containing 0.8 mole fraction of ethanol  $\text{EtOH}$  is distilled completely at 760 mm. (a) What is the composition of the first vapor to come off? (b) Of the last drop of liquid to evaporate? (c) What would be the values of the above quantities if the distillation were carried out in a cylinder provided with a piston so that none of the vapor could escape?

$N_{\text{ethanol}}$ liquid	$N_{\text{ethanol}}$ vapor	Temperature	$N_{\text{ethanol}}$ liquid	$N_{\text{ethanol}}$ vapor	Temperature
0	0	77.15	0.563	0.507	72.0
0.025	0.070	76.7	0.710	0.600	72.8
0.100	0.164	75.0	0.833	0.735	74.2
0.240	0.295	72.6	0.942	0.880	76.4
0.360	0.398	71.8	0.982	0.965	77.7
0.462	0.462	71.6	1.00	1.0000	78.3

14. The boiling point of the immiscible liquid system, naphthalene-water, is 98° under a pressure of 733 mm. The vapor pressure of water at 98° is 707 mm. Calculate the per cent of naphthalene in the distillate.

15. Using the following data for cadmium nitrate in water plot the integral heats

of solution,  $\Delta H_{\text{int}}$  against the molality,  $m$ , and determine the differential heat of solution of cadmium nitrate in a 4 molal solution.

$m$ (molality)	1.063	1.799	2.821	4.251	6.372	9.949
$\Delta H_{\text{int.}}$ (joules)	-34.2	-56.7	-88.3	-126.0	-174.4	-228.5

16. The integral heat of solution of 1 mole of  $\text{H}_2\text{SO}_4$  in  $n$  moles of water is given by the formula:

$$\Delta H_{\text{solution}} = \frac{-17,860n}{n + 1.798} \text{ cal.}$$

Calculate  $\Delta H$  for the following reactions:

- Solution of 1 mole of  $\text{H}_2\text{SO}_4$  in 5 moles of water.
- Solution of 1 mole of  $\text{H}_2\text{SO}_4$  in 10 moles of water.
- Solution of 1 mole of  $\text{H}_2\text{SO}_4$  in a large excess of water, 100,000 moles for example.
- Addition of a large excess of water to a solution containing 1 mole of  $\text{H}_2\text{SO}_4$  in 10 moles of water.
- Addition of 5 moles of water to a solution containing 1 mole of  $\text{H}_2\text{SO}_4$  in 5 moles of water.

17. Ten grams of carbon tetrachloride (density = 1.595) and 50 g. of benzene (density = 0.878) are mixed. Calculate the composition of the mixture in terms of (a) per cent by weight of each compound, (b) mole fractions, (c) molal concentration, and (d) molar concentration, considering the benzene to be the solvent, assuming for this calculation that the solution is ideal.

18. In an evacuated vessel of 6-liter capacity, 1.0 g. of water and 1.0 g. of hexane are evaporated and heated to  $350^\circ$ .

- What is the total pressure in atmospheres?
- What is the mole fraction of water in the vapor?
- What is the percentage composition (by weight) of the vapor?

19. Three flasks are connected by stopcocks. Given the following data

Flask	Volume (liters)	Contents	Pressure (atm.)
A	1	$\text{O}_2$	2
B	2	$\text{N}_2$	1
C	3	$\text{H}_2$	3

Calculate: (a) total pressure, (b) partial pressure of each gas, and (c) mole fraction of each gas after the stopcocks are opened and the gases are mixed at constant temperature.

20. A 10-liter tank of methane at 740 mm. total pressure and  $25^\circ$  contains 1 liter of water. How many grams of methane are dissolved in the water?

21. The Henry's constant  $K$  for nitrogen in water at  $25^\circ$  is  $6.51 \times 10^7$  and for helium it is  $1.12 \times 10^8$ . Calculate the number of milliliters of nitrogen liberated from 1 kg. of water when the pressure on the nitrogen in equilibrium with the water is reduced from 5000 mm. to 760 mm. Calculate the number of milliliters of helium liberated under the same conditions. The difference finds application in deep-sea diving.

22. The reduction in solubility of gases such as carbon dioxide in aqueous solutions by inorganic salts is, within experimental errors, an additive function of ion concentrations. Using this fact, calculate, from the following data, the solubility of carbon dioxide in a 0.1  $M$  solution of sodium nitrate at  $25^\circ$ . The solubilities are



expressed in terms of volume of gas measured at 0° and 760 mm. per volume of solution at 25°.

## DATA AT 25°

<i>Solution</i>	<i>Solubility CO<sub>2</sub></i>
pure H <sub>2</sub> O	0.7567
0.1 M KCL	0.7432
0.1 M NaCl	0.7379
0.1 M KNO <sub>3</sub>	0.7501

23. At 25° the vapor pressures of chloroform and carbon tetrachloride are 199.1 and 114.5 mm. respectively. If the two liquids form an ideal solution: (a) what is the composition of the vapor in equilibrium with a mixture containing 1 mole of each; (b) what is the vapor pressure of the mixture?

24. For mixtures of benzene and isopropanol the following data are available at 25°. Draw a complete pressure-composition diagram including partial pressure curves for each of the constituents. What would be the approximate composition of distillate obtained by distilling a liquid whose mole fraction (with respect to isopropanol) was 0.521 until its mole fraction had become 0.70? The vapor pressure of pure benzene at 25° is 94.4 mm.

<i>Mole fraction of isopropanol</i>		<i>Partial pressure of isopropanol in mm</i>
<i>In liquid</i>	<i>In vapor</i>	
0.000	0.000	....
0.059	0.123	12.9
0.146	0.205	22.4
0.362	0.255	27.6
0.521	0.288	30.5
0.700	0.365	36.4
0.836	0.470	39.5
0.926	0.635	42.2
1.000	1.000	44.0

25. When nitric acid is dissolved in water heat is evolved, and the amount of the heat per mole of nitric acid varies with the concentration as given by the formula

$$\Delta H = \frac{-8.974n}{n + 1.737} \text{ kcal.}$$

where  $n$  is the number of moles of water to which the 1 mole of nitric acid is added. Calculate the heat change involved in the addition of (a) 1 mole of nitric acid to a liter of water, (b) 1 mole of nitric acid to a large excess of water, and (c) 100 g. of nitric acid to 100 g. of water.

26. With the formula given in the preceding problem calculate  $\Delta H$  for various values of  $n$  (1, 3, 5, 10, and 20); plot the data, and draw a smooth curve. Draw a tangent to the curve where  $n = 6$  and determine its slope. Differentiate the expression and calculate the differential heat of solution of water, i.e., the differential heat of dilution, at this concentration and compare it with the slope of the tangent.

27. The dissolved air described in Problem 3 is expelled by boiling into an evacuated space. When this mixture of 34.65 per cent oxygen and 65.35 per cent nitrogen

by volume is redissolved in water at  $20^\circ$  under atmospheric pressure what is the composition of the dissolved gas?

28. At a total pressure of 240.7 mm. a certain liquid steam distils at  $70^\circ$ , the distillate containing 19.42 per cent of the liquid.

(a) What is the molecular weight of the liquid?

(b) When the total pressure is 730.3 mm. the liquid distils over with steam at  $98^\circ$ . Calculate the normal boiling point of the liquid. Necessary values for the vapor pressure of water are to be found in tables.

29. Two 2-liter vessels are connected with a tube and stopcock of negligible volume. Initially the first bulb contains 10 g. of water and is at  $10^\circ$ . The other bulb contains 5 atm. of  $\text{NH}_3$  and is at  $0^\circ$ . Calculate the total pressure in the system when the stopcock is opened and the whole apparatus is brought to equilibrium at  $25^\circ$ . The solubility of  $\text{NH}_3$  in water at  $25^\circ$  is 27.011 moles per 1000 g.  $\text{H}_2\text{O}$ . Neglect second-order effects.

30. In the system isopropyl ether-isopropanol the vapor and liquid have the following compositions of isopropyl ether:

		<i>Mole fraction isopropyl ether</i>								
In liquid	0	0.084	0.19	0.44	0.66	0.75	0.78	0.88	0.95	100
In vapor	0	0.30	0.45	0.64	0.73	0.76	0.78	0.84	0.91	100

Plot the data and state whether this system exhibits a minimum or maximum boiling point. If so, which? What is the composition of this mixture of maximum or minimum boiling point? With a rough sketch show what the temperature-composition diagram would look like.

## CHAPTER X

### SOLUTIONS OF NON-VOLATILE SOLUTES

When only one of the components in a liquid system is volatile, as in an aqueous solution of sugar, both the measurements and the theoretical calculations are simplified. The total pressure of the system gives at once the partial pressure of the volatile component. The solute or solutes play no part in the measurements except in so far as they affect the escaping tendency, i.e., the vapor pressure, of the solvent. Because the vapor pressure is lowered, the boiling point is raised and the freezing point is lowered. The phenomenon of osmosis is connected also with the lowering of the vapor pressure. All four of these properties are interrelated, and they are used for calculating molecular weights and other properties of dissolved substances.

From a kinetic point of view, the lowering of the vapor pressure may be explained as due to solute molecules reducing the effective concentration of the solvent. Accordingly, it is the number of molecules or separate units, rather than their kind, which determines the extent of the vapor pressure lowering.

**Lowering of the Vapor Pressure.** Raoult's law is the fundamental formula for connecting the concentration of the solute with the vapor pressure of the solvent. In fact, Raoult first applied it to the lowering of the vapor pressure by various non-volatile solutes and expressed it in the statement that the lowering of the vapor pressure divided by the vapor pressure of the pure solvent is equal to the mole fraction of the solute.

As given in the last chapter the equation

$$p_{\text{solvent}} = N_{\text{solvent}} p_{\text{solvent}}^0 \quad [1]$$

is applicable to ideal solutions, but the equation holds well for non-ideal solutions also if they are dilute, because the solvent is only slightly changed from its normal behavior by the addition of a small amount of solute to it.

The difference between two quantities can often be determined more accurately than the absolute value of one of them. According to this principle the difference between the vapor pressure of the solutions and that of the pure solvent can be determined and calculated much more easily and accurately than the vapor pressure of the solu-

tion. The percentage error then applies only to a small correcting term. Writing equation (1) in the equivalent form for the solvent

$$p = N_1 p^0 = \frac{n_1}{n_1 + n_2} p^0$$

where  $p$  is the vapor pressure of the solution (or rather the partial pressure of the solvent in solution),  $p^0$  is the vapor pressure of the pure solvent and  $n_2$  is the number of moles of solute;  $n_1$  is the number of moles of solvent, and  $N_1$  is the mole fraction of the solvent in the solution. Rearranging terms it can be shown that

$$\frac{p^0 - p}{p^0} = \frac{n_2}{n_1 + n_2} = N_2 \quad [2]$$

where  $N_2$  is the mole fraction of the solute.

*Example 1.* Raoult\* found that when 2.47 g. of ethyl benzoate were dissolved in 100 g. of benzene at 80° the vapor pressure was lowered from 751.9 to 742.6 mm. Calculate the molecular weight  $M_2$  of ethyl benzoate from these data. The molecular weight of benzene is 78.1.

$$\begin{aligned} \frac{p^0 - p}{p^0} &= \frac{n_2}{n_2 + n_1} \\ \frac{751.9 - 742.6}{751.9} &= \frac{2.47/M_2}{2.47/M_2 + 100/78.1} \\ M_2 &= 154 \end{aligned}$$

The molecular weight obtained by adding together the atomic weights is 150.2. If the solution were more dilute, its behavior would be more nearly ideal and the calculated value would check better with the correct value.

The molecular weight may be calculated as well by equation (1) as by equation (2) but the mathematical operations must be carried out with greater precision. Thus with a slide rule the calculation by equation (1)

$$742.6 = \frac{100/78.1}{100/78.1 + 2.47/M_2} \times 751.9$$

may give for  $M_2$  a value anywhere between 130 and 180. However, with a five-place logarithm table the calculation gives 154, as obtained by equation (2). Equation (2) is better than (1) because it applies to  $(p^0 - p)$  rather than to  $p^0$ . It is often advantageous to apply calculations to a small correcting term rather than to the large quantity itself.

The vapor pressures of the solution may be determined by static methods in which the pressure is read directly with a manometer. A

\* Raoult, *Z. physik. Chem.*, **2**, 371 (1888).

differential manometer is convenient for measuring the difference between the vapor pressure of the solution and that of the pure material used as the solvent, one arm of the  $U$  being connected with the solution and the other with the solvent. An oil or other liquid of low density is used as the manometer liquid and the difference in vapor pressure is read directly on the manometer. Both liquids must be boiled out to remove any dissolved air which might later lead to an abnormal pressure.

In another method a solution in one dish is allowed to come to equilibrium with a solution of a standard substance in another dish.\* The two are placed in an enclosed, thermostated vessel until there is no further loss or gain of weight, and then it is known that both solutions have the same vapor pressure. The concentration of the standard substance, potassium chloride, for example, is determined with a refractometer or by other means and the vapor pressure calculated from a previously determined relation between the vapor pressure and the concentration of the standard solution.

The gas saturation method described on page 153 is suitable also for determining the vapor pressure of solutions. The loss in weight of the solution is determined after bubbling through a known volume of an inert gas, or the vaporized solvent is caught in an absorption tube and weighed or titrated. Again, more accurate results can be obtained with a differential method because errors involving the absolute measurements of volume, temperature, and other variables tend

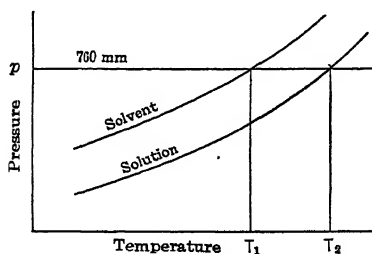


FIG. 63

to cancel out. The measurements are made first on the pure solvent and then on the solution. Accurate measurements have been made with this method on the lowering of the vapor pressure of a solute.†

#### Elevation of the Boiling Point.

Since the vapor pressure of a solvent is lowered by the addition of a non-volatile solute, it is obvious

that the solution must be heated to a higher temperature than the solvent in order that both may have the same vapor pressure. This fact is shown in Fig. 63, where the curve for the vapor pressure of the solution is seen to cut the line of barometric pressure at a higher temperature than does the curve representing the vapor pressure of the

\* Robinson and Sinclair, *J. Am. Chem. Soc.*, **56**, 1830 (1934).

† Washburn and Heuse, *J. Am. Chem. Soc.*, **37**, 309 (1915).

solvent. Then  $p$  is the pressure (760 mm.) at which both the solvent and the solution boil,  $T_1$  is the boiling temperature of the solvent at this pressure, and  $T_2$  the boiling point of the solution.

This elevation of the boiling point  $T_2 - T_1$  or  $\Delta T_b$  is directly connected with the change in the vapor pressure  $p$  and, accordingly, with the change in concentration of the solution.

By the Clausius-Clapeyron equation (page 157)

$$\frac{dp}{dT} = \frac{pL_v}{RT^2} \quad [3]$$

where  $L_v$  is the heat of vaporization per mole.

$$\text{For small changes} \quad \Delta T = \frac{RT^2}{pL_v} \Delta p \quad [4]$$

$$\text{and by Raoult's law} \quad \frac{\Delta p}{p} = \frac{n_2}{n_1 + n_2}$$

$$\text{Then} \quad \Delta T = \frac{RT^2}{L_v} \times \frac{n_2}{n_1 + n_2} \quad [5]$$

In dilute solutions the change in boiling point is so small that  $\Delta T$  may be substituted for the differential  $dT$  in equation (3), but it must be remembered that the resulting formula cannot be used over large concentration ranges. Also, in dilute solutions,  $n_2$  is negligible in comparison with  $n_1$ , and equation (5) becomes

$$\Delta T_b = \frac{RT^2}{L_v} \times \frac{n_2}{n_1} \quad [6]$$

Since

$$\frac{n_2}{n_1} = \frac{m}{1000/M_1}$$

where  $m$  is the molality of the solution and  $M_1$  is the molecular weight of the solvent, equation (6) becomes

$$\Delta T_b = \frac{RT^2 M_1}{1000 L_v} m \quad [7]$$

or

$$\Delta T_b = K_b m \quad [8]$$

where  $K_b$  is a constant characteristic of the solvent and is given by

$$K_b = \frac{RT^2 M_1}{1000 L_v} \quad [9]$$

These relations show that in dilute solution the elevation of the boiling point is proportional to the concentration of the solute, and this direct proportionality has been abundantly verified by many experiments.

$K_b$  is called the molal elevation of the boiling point. However, it must be emphasized that this molal boiling-point constant is not the actual elevation for a 1-molal solution, for in such a concentrated solution the assumptions made in deriving equation (8) would not be valid. For example, the neglect of  $n_2$  in the denominator of equation (5) causes an error of 1.8 per cent in a 1-molal solution.  $K_b$  is rather a hypothetical value calculated for a 1-molal solution on the basis of the laws of dilute solutions. It may be evaluated from the thermodynamic quantities in (9) or experimentally by measurement of the rise in boiling point produced by a small, known concentration of a solute whose molecular weight is known. The values of  $K_b$  obtained thermodynamically agree closely with those obtained experimentally.

*Example 2.* Find the molal boiling-point constant for water, which boils at  $100^\circ$  with the absorption of 539.7 cal. per gram.

$$K_b = \frac{1.987 \times 373.1^2 \times 18.02}{1000 \times (539.7 \times 18.02)} = 0.513$$

In practical problems where  $w_2$  grams of solute having a molecular weight of  $M_2$  is added to  $w_1$  grams of solvent, equation (8) becomes

$$\Delta T_b = K_b m = K_b \frac{w_2}{M_2} \frac{1000}{w_1} \quad [10]$$

*Example 3.* What is the boiling point of a solution containing 90 g. of water and 2.00 g. of cane sugar (molecular weight = 342)?

$$\Delta T_b = K_b \frac{w_2}{M_2} \frac{1000}{w_1} = 0.513 \times \frac{2.00}{342} \times \frac{1000}{90.0} = 0.0333$$

$$\text{Boiling point} = 100 + 0.033 = 100.033^\circ$$

**Experimental Determination of Boiling Points.** The importance of molecular weights in establishing the formulas of new compounds has been discussed in an earlier chapter. Frequently it is impossible to vaporize the material for a vapor-density measurement on account of thermal decomposition. The molecular weight  $M_2$  may then be determined from the elevation of the boiling point  $\Delta T_b$  which is produced by dissolving the material in a suitable solvent. Calculations are made with the help of equation (10). The molal boiling-point constants for several solvents are given on page 213.

The accurate determination of the elevation of the boiling point has been the object of considerable investigation. The temperature of the

boiling solution and not that of the vapor is desired. Therefore the thermometer bulb must be placed directly in the liquid. The liquid, however, is likely to become superheated and register a temperature considerably above its true boiling point. This difficulty has been met by heating the solution locally with electrically heated wires immersed in the solution. Small bubbles of vapor are formed which prevent superheating. In another method, a spray of solution and vapor is directed on the thermometer bulb above the main body of the liquid. In rising through the tubes leading to the thermometer the solution and vapor come to equilibrium.

A weighed quantity of solute is introduced into a weighed quantity of solvent. Or, in a better technique, samples are withdrawn and analyzed by chemical or physical means. Since the boiling point is affected by changes in the atmospheric pressure, the determinations on the solution and solvent must be made simultaneously in two pieces of apparatus, or over such short periods of time that the barometer fluctuations are negligible. In accurate work a barostat may be used to maintain a fixed pressure for all determinations. By automatic regulation with an electrical circuit, compressed air is admitted into a chamber whenever the mercury monometer falls below a predetermined pressure. The need of these precautions is evident from the fact that a change of 0.03 or 0.04 mm. changes the boiling point of most solvents by  $0.001^{\circ}$ .

#### Lowering of the Freezing Point.

It has long been known that the freezing point of water, or other liquid, is lowered by the addition of a solute, and it was pointed out by Blagden more than a century ago that the depression of the freezing point is directly proportional to the concentration of the solution. The reason for the lowering will be understood with the help of Fig. 64.

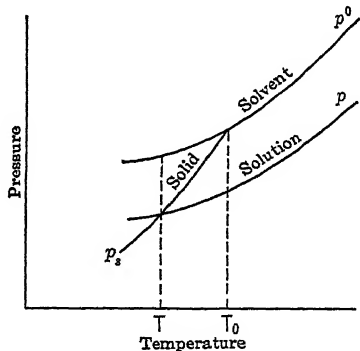


FIG. 64

At the freezing point the solid and the liquid are in equilibrium and both must have the same vapor pressure. If the solid has a greater pressure than the liquid, it will distil over into the liquid phase; if the liquid has the greater pressure, it will change into the solid. When solid and liquid solvent are in equilibrium and a solute is dissolved in the liquid, the solid solvent will disappear if the temperature is maintained constant, but the disappearance of the solid may be stopped and a state of equilibrium



may be effected by lowering the temperature. It will be remembered that the vapor pressure-temperature curve of a solid is steeper than that of the corresponding liquid because the heat of sublimation of the solid is greater than the heat of vaporization of the liquid. At the intersection of the two curves, solid and liquid are in equilibrium, and the corresponding temperature is the freezing point. The greater the concentration of the solution, the lower is the vapor-pressure curve and the lower is the freezing point of the solution, i.e., the temperature at which the vapor curve of the solution intersects the vapor curve for the ice.

The quantitative relation between the concentration of the solution and the freezing-point depression can be derived as follows:

Let  $p_s$  be the vapor pressure of the pure solid solvent (ice in the case of water), let  $p$  be the vapor pressure of the solution and let  $p^0$  be the vapor pressure of the pure solvent in the liquid state. The derivation is limited to solutions in which the solvent freezes out as a pure solid unmixed with the solute. (Most solutions, including aqueous ones, freeze in this manner, but in some cases a solid solution is formed as described later on page 329.) By Raoult's law, which holds in dilute solutions,

$$p = p^0 N_1$$

where  $N_1$  is the mole fraction of the solvent. At the freezing point of the solution a state of equilibrium exists and

$$p_s = p = p^0 N_1$$

Then, differentiating with respect to temperature,

$$\frac{dp_s}{dT} = N_1 \frac{dp^0}{dT} + p^0 \frac{dN_1}{dT} \quad [11]$$

Substituting for  $\frac{dp_s}{dT}$  and  $\frac{dp^0}{dT}$  in equation (11) their equivalents in terms of the heat of sublimation of the solid solvent  $L_s$  and the heat of vaporization of the liquid solvent  $L_v$  as given by the Clausius-Clapeyron equation

$$\begin{aligned} \frac{dp}{dT} &= \frac{Lp}{RT^2} \\ \frac{L_s p_s}{RT^2} &= N_1 \frac{L_v p^0}{RT^2} + p^0 \frac{dN_1}{dT} \end{aligned} \quad [12]$$

Remembering that  $p_s = p^0 N_1$ , cancelling out equivalent terms and rearranging

$$\frac{L_s - L_v}{RT^2} = \frac{d \ln N_1}{dT} \quad [13]$$

The heat of fusion  $L_f$  is equal to the difference between the heat of sublimation and the heat of vaporization. Then

$$\frac{L_f}{RT^2} = \frac{d \ln N_1}{dT} \quad [14]$$

Integrating between the limits,  $T$ , corresponding to a solution, and  $T_0$ , corresponding to the pure solvent where  $N_1 = 1$ ,

$$\frac{L_f}{R} \int_T^{T_0} \frac{dT}{T^2} = \int_{N_1}^1 d \ln N_1$$

and

$$\frac{L_f(T_0 - T)}{RT_0 T} = -\ln N_1 \quad [15]$$

This is an exact equation for solutions which obey Raoult's law, provided that the heat of fusion,  $L_f$ , is constant between  $T_0$  and  $T$ , and that the vapor obeys the simple gas law.

In a binary solution which contains only one solute and one solvent, the mole fraction of the solvent  $N_1$  is equal to  $1 - N_2$ , where  $N_2$  is the mole fraction of the solute. In dilute solutions a simplification may be made. Expanding by MacLaurin's series

$$-\ln N_1 = -\ln (1 - N_2) = N_2 + \frac{1}{2} N_2^2 + \frac{1}{3} N_2^3 + \dots \quad [16]$$

and remembering that for small values of  $N_2$  the higher powers may be neglected as an approximation in comparison with the first power,\*

$$-\ln N_1 = -\ln (1 - N_2) \cong N_2$$

and substituting into equation (15)

$$N_2 = \frac{L_f (T_0 - T)}{RT_0 T_1} \quad [17]$$

Designating the freezing point depression  $T_0 - T$  by  $\Delta T_f$  and remembering that since  $N_2$  is small,  $T_0$  and  $T$  are nearly the same, equation (15) may be written in an approximate form as

$$\Delta T_f = \frac{RT_0^2}{L_f} N_2 = \frac{RT_0^2}{L_f} \frac{n_2}{n_1 + n_2}$$

\* For example, if  $N_2 = 0.01$  the expression becomes  $0.01 + \frac{1}{2}(0.0001) + \frac{1}{3}(0.000001)$ , which is equal to 0.01 within one-half of one per cent.

For dilute solutions the number of moles of solute  $n_2$  is small compared to the number of moles of solvent  $n_1$  and

$$\Delta T_f = \frac{RT_0^2}{L_f n_1} n_2. \quad \text{Also, as before } \Delta T_f = K_f m \quad [18]$$

where  $\frac{n_2}{n_1}$  is given in terms of the molality  $m$ , and the molecular weight  $M_1$  of the solvent

$$\frac{n_2}{n_1} = \frac{m}{1000/M_1}$$

$$K_f = \frac{RT_0^2}{L_f \times (1000/M_1)} \quad [19]$$

According to this relation, in dilute solutions, the lowering of the freezing point is directly proportional to the molality  $m_2$  of the solute. Experimental facts are in agreement with this formula, and it is clear why the simple proportionality fails in the more concentrated solutions.

The proportionality constant  $K_f$  is called the freezing point constant or the molal depression.

*Example 4.* For water  $K_f$  has the value  $1.86^\circ$ , calculated as follows:

$$K_f = \frac{RT_0^2 M_1}{L_f \times 1000} = \frac{1.987 \times 273.1^2 \times 18.02}{(18.02 \times 79.7) \times (1000)} = 1.86$$

According to this equation a normal solute added to 1000 g. of water will lower the freezing point at the rate of  $1.86^\circ$  per mole, but the relation holds only for dilute solutions. Even a 1-molal solution is too concentrated, and the depression will be something less than  $1.86^\circ$ . In very concentrated solutions the behavior may become quite complex.

The molecular weight can be determined from the freezing point depression using the following formula, similar to equation (10),

$$\Delta T_f = K_f \frac{w_2}{M_2} \frac{1000}{w_1} \quad [20]$$

The freezing point constant like the boiling point constant may be evaluated by direct experiment with a solute of known molecular weight.

The freezing point constants and boiling point constants are given in Table I for a number of different solvents.

Equation (15) may be written in the form

$$\ln N_1 = \frac{L_f}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \quad [21]$$

where  $T_0$  is the freezing point of the solvent,  $T$  the freezing point of

TABLE I  
MOLAL FREEZING-POINT AND BOILING-POINT CONSTANTS

Solvent	Freezing Point	$K_f$	Boiling Point	$K_b$
Acetic acid	17	3.9	118.1	2.93
Acetone	....	....	56.0	1.71
Benzene	5.4	5.12	80.2	2.53
Chloroform	....	....	60.2	3.63
Ethanol	....	....	78.3	1.22
Ethylene bromide	10	12.5	....	....
Ethyl ether	....	..	34.4	2.02
Heptachloropropane	29.5	12.0	....	....
Naphthalene	80	6.8	....	....
Tribromophenol	95	20.4	....	....
Water	0	1.855	100	0.51

the solution and  $N_1$  the mole fraction of the solvent. As such, it finds application in the study of solutions. When  $\log N_1$  is plotted against  $1/T$ , a straight line is produced if the heat of fusion is independent of temperature, if the solution is ideal and if the solid separates as a pure component.

**Experimental Determination of Freezing Points.** Freezing-point depressions can be determined with great accuracy. Measurements of moderate accuracy may be made easily with simple apparatus. The freezing points of the pure solvent and the solution are determined with an accurate thermometer. A tube containing the solution is jacketed and immersed in a bath of ice and salt. It is provided with a stopper through which operates an efficient ring stirrer. The temperature gradually falls until the solid appears, and the first steady temperature is recorded as the freezing point.

In order to obtain trustworthy results with the freezing-point method, it is necessary that only the pure solvent separate out when the solution freezes and that excessive overcooling be avoided. Sometimes it is necessary to introduce a small crystal of the solid solvent in order to prevent supercooling. When too great supercooling occurs, the subsequent freezing of the solution results in the separation of such a large amount of solvent in the solid state that the solution becomes considerably more concentrated than the original solution. The best results are obtained, however, not by weighing out a solute to give a definite concentration but by analyzing the solution which is in equilibrium with the solid solute. Under these conditions the supercooling of the solution introduces no difficulties.

The most accurate results are obtained with two vacuum-jacketed vessels placed in an ice bath and partly filled with cracked ice, as shown in Fig. 65. One vessel contains solvent; the other solution. The difference in temperature is measured to one ten-thousandth of a degree with a multiple-junction thermoelement and sensitive potentiometer. The two liquids are stirred vigorously, and the concentration of the solution in equilibrium with the ice is determined accurately by chemical analysis or by physical measurements, for example, with a refractometer.

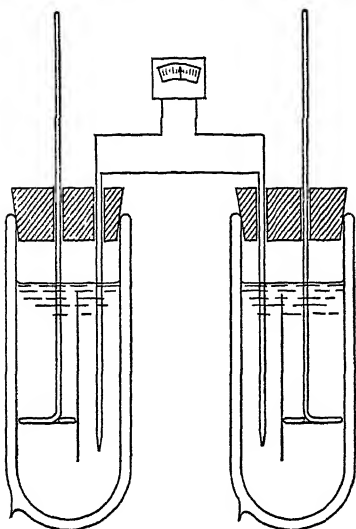


FIG. 65

Table II gives a series of results on aqueous solutions of mannitol measured in this way. The close agreement between observed depressions and the depression as calculated by equation (19) lends proof to the validity of the freezing-point laws.

TABLE II

FREEZING POINTS OF AQUEOUS SOLUTIONS OF MANNITOL<sup>1</sup>

Concentration in Millimoles per 1000 g. H <sub>2</sub> O	$\Delta T_f$ (obs.)	$\Delta T_f$ (calc.)
4.02	0.0075	0.0075
8.42	0.0157	0.0156
14.04	0.0260	0.0261
28.29	0.0525	0.0525
62.59	0.1162	0.1162

<sup>1</sup> Adams, *J. Am. Chem. Soc.*, **37**, 481 (1915).

**Osmosis.** Closely related to the lowering of the freezing point and the lowering of the vapor pressure is the phenomenon of osmosis, i.e., the passage of a solvent through a membrane from a dilute solution into a more concentrated one. This phenomenon was first observed in 1748 by Abbé Nollet. If sufficient pressure is applied to the more concentrated solution (by means of a piston, a column of mercury, or a column of the solution itself) the passage of solvent will reverse

direction. If one of the liquids is the pure solvent, the difference in the pressure on the solution and on the pure solvent which will cause the flow of solvent to stop is the *osmotic pressure* of the solution.

Many theories have been proposed to explain the passage of solvent through a semi-permeable membrane from a dilute solution to a more concentrated one. From a thermodynamic standpoint the solvent merely moves from a region where its escaping tendency is large (its vapor pressure is high) to a region where its escaping tendency is small. The membrane is so constituted that the dissolved material cannot pass. The presence of the dissolved material lowers the escaping tendency of the solvent, and the greater the concentration, the greater is the lowering.

A simple illustration is offered by putting a dish containing pure water and one containing a solution of sugar or other material into an empty desiccator, and immersing it in a thermostat. After standing, the level of the solution will rise and that of the pure water will fall owing to the diffusion of the water vapor from the pure solvent, where the vapor pressure is high, to the solution, where the vapor pressure is relatively low.

One of the ways in which a semi-permeable membrane may function is shown schematically in Fig. 66. Very small passages exist in the semi-permeable membrane, so small that the liquids are kept from flowing through by surface tension, even if a large hydrostatic pressure is applied. But the solvent molecules can still pass through in the vapor phase as individual molecules, and there will be a steady migration from the solvent to the solution as indicated by the arrows representing vapor pressures—the heavier arrow indicating the higher vapor pressure of the solvent. The solute cannot pass through by this mechanism since it is non-volatile. That this mechanism is possible has been proved by the osmosis which occurs when a solution is separated from a solvent by a glass tube containing many infinitesimal cracks.

Many semi-permeable membranes are more complex than systems of minute passages, available for gas diffusion but not for liquid diffusion. Animal membranes and certain gels offer a medium for the

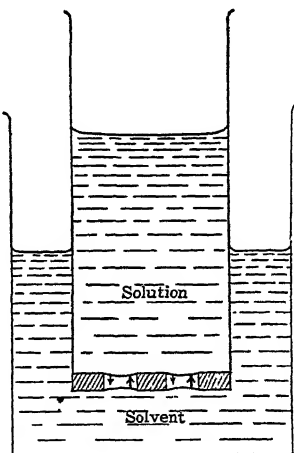


FIG. 66

diffusion of water but not for the diffusion of the solute. Solubility of the solvent in the membrane provides another way in which a semi-permeable membrane may operate. For example, if a rubber membrane separates a solution of sugar in pyridine from pure pyridine, the pyridine dissolves in the rubber and passes through from the solvent into the solution.

Ostwald demonstrated theoretically that the pressure due to osmosis must be independent of the nature of the membrane employed in measuring it. Thus, in Fig. 67, *A* and *B* represent two different semi-permeable membranes in an imaginary apparatus. If the nature of the membrane has any influence on the osmotic pressure, the osmotic pressure  $P_B$  may be imagined greater than the osmotic pressure  $P_A$ .

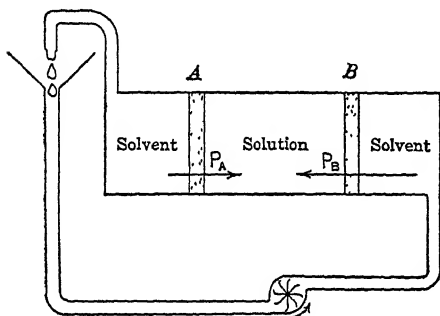


FIG. 67

Under this condition the flow in the compartment between the membranes will be to the left from *B* to *A*, and the solvent may be returned to the right through a turbine which may be made to do mechanical work. After being returned to the compartment at the right it will flow into the solution and thence through the cycle repeatedly. But such an arrangement would be a means of producing energy at constant temperature in a cyclic process. Since such perpetual motion is contrary to experience, the premise of two different membranes must be wrong, and it is concluded that all semi-permeable membranes give the same osmotic pressure.

In actual practice different membranes may appear to give different hydrostatic pressures, but if sufficient time is allowed for the attainment of equilibrium, and if the membrane does not leak, the pressures ultimately will be the same. The nature of the membrane and its area determine how *rapidly* osmosis occurs but not the osmotic pressure. If any solute diffuses through the membrane, the membrane is not truly semi-permeable. Examples of dialysis where certain solutes diffuse through and others do not will be discussed later (page 234).

**Osmotic Pressure.** The first direct measurements of osmotic pressure were made by the botanist, Pfeffer, in 1877. Using a mercury manometer he was able to measure the hydrostatic pressure generated in a solution by the ingress of water through a semi-permeable mem-

brane without serious dilution of the solution. Pfeffer's results are given in Tables III and IV. The approximate volume of solution holding 1 g. of cane sugar is given under  $v$ , the osmotic pressure in atmospheres under  $P$ , and the absolute temperature under  $T$ .

TABLE III

RELATION OF OSMOTIC PRESSURE TO CONCENTRATION AT 287°

$v$ (ml.)	$P$ (atm.)	$Pv$
100	0 70	70
50	1 34	67
25	2 74	68
16 5	4 10	68

TABLE IV

RELATION OF OSMOTIC PRESSURE TO TEMPERATURE

(Approximately 1 g. per 100 ml. of solution)

$T$ (°K.)	$P$ (atm.)	$P/T$
273.0	0 649	0 00238
279 8	0.664	0.00237
286.7	0.691	0 00241
288.5	0 684	0 00237
295 0	0 721	0.00244
305 0	0.716	0 00235
309.0	0.746	0.00241

The significance of Pfeffer's measurements was first perceived by van't Hoff,\* who pointed out the existence of a striking parallelism between the properties of gases and the osmotic properties of solutions. As shown in Table III, the product  $Pv$  is a constant, just as it is for gases according to Boyle's law. As shown in Table IV, the pressure is proportional to the absolute temperature just as it is for gases, i.e.,  $P/T = \text{constant}$ .

Moreover, the two relations may be combined to give the same constant  $R$  as is obtained for gases,

$$Pv = n RT = \frac{g}{M} RT \quad [22]$$

\* Van't Hoff, *Z. physik. Chem.*, 1, 481 (1887).



where  $P$  is osmotic pressure,  $v$  is the volume of the solution, and  $g$  is the weight of solute having molecular weight  $M$ .

*Example 5.* From Pfeffer's data in Table IV, it is seen that 1 g. in 100 ml. or 1 mole (342 g.) in 34.2 liters gives an osmotic pressure of 0.649 atm. at 0°.

Then

$$R = \frac{Pv}{T} = \frac{0.649 \times 34.2}{273} = 0.0813 \text{ liter-atm. per degree}$$

Within the limits of the experimental error this is the same as the gas constant  $R$ , viz., 0.08206, and the standard equation used for making calculations on gases can thus be used for calculating approximate osmotic pressures.

*Example 6.* If 2.00 g. of sugar having a molecular weight of 342 is dissolved in 50 ml. of solution at 25° what will be the osmotic pressure?

$$P = \frac{g}{M} \frac{RT}{v} = \frac{2.00 \times 0.08205 \times 298.1}{342 \times 0.0500} = 2.86$$

This formula holds only for dilute solutions where the volume of the solute is negligible in comparison with that occupied by the solvent.

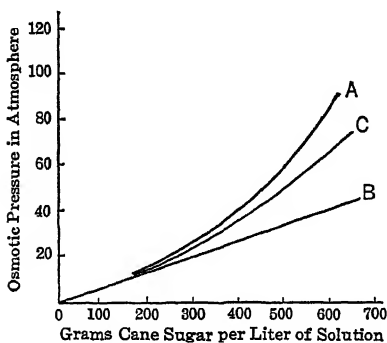


FIG. 68

Results of Berkeley and Hartley\* up to 100 atm. osmotic pressure are shown diagrammatically in Fig. 68. Curve A represents the actually observed osmotic pressure, and the other two curves represent pressures calculated from the equation  $Pv = nRT$ . In curve B,  $v$  denotes the volume of the whole solution; in curve C it denotes only the volume of the solvent. It is evident that curve C gives much better results than curve B, and that the volume of the solvent is more significant

than that of the solution. It is clear, however, that both curves, B and C, fail to express the true behavior in concentrated solutions.

This discrepancy between experiment and theory in concentrated solutions is not peculiar to osmotic pressure. Ideal solutions are very rare, and we have to accept the fact that the behavior of concentrated solutions is too complicated to be explained by the simple laws which we have thus far developed. Undoubtedly the nature of the solvent itself is affected by the presence of a high concentration of solute. In dilute solutions either formula is satisfactory.

\* Berkeley and Hartley, *Trans. Roy. Soc. A* 206, 481 (1906).

**Comparison of Experimental Methods.** The four properties of solutions which have just been studied, vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure, are closely connected. The freezing-point depression can be measured most accurately and most easily, whereas the osmotic pressure can be measured least accurately and only with difficulty. The freezing-point method is limited to low temperatures where the solubility is often small. The boiling-point readings may be seriously affected by fluctuations in the barometric pressure and, in water, the molal elevation is only about one-third as great as the freezing-point depression. The temperature range is limited also in the boiling-point method. The vapor-pressure lowering is adaptable to different temperatures and capable of high accuracy, but it requires more elaborate apparatus. Osmotic pressure was most used in the early development of the theory of solutions and it is the most important historically, but at present the concept of vapor-pressure lowering is much more useful in the theoretical treatment of solutions.

**Free Energy of Dilution.** The properties of a system are conveniently and quantitatively defined in terms of energy. In the study of solutions, for example, the free energy of dilution is a useful thermodynamical quantity. The free energy of dilution may be calculated by means of formula (23), which holds true at constant temperature for a system doing no work other than expansion work, as shown on page 134.

$$dF = v dp \quad [23]$$

A large reservoir of solution having a vapor pressure  $p$  is placed near a reservoir of pure solvent having a vapor pressure  $p^0$ . The temperature  $T$  is kept constant throughout. One mole of solvent is vaporized from the solution by keeping the pressure infinitesimally less than  $p$ . The quantity of solution is so great that the removal of 1 mole of solvent does not appreciably increase the concentration of the solution. Since the process is carried out reversibly at constant temperature and pressure the free energy change for process I is zero.

(I) 1 mole of solvent in solution  $\rightarrow$  1 mole solvent as vapor

The mole of vapor is placed in a cylinder provided with a piston and compressed reversibly (i.e., by infinitesimal increases of pressure) until its pressure is  $p^0$ . This process may be written as (II).

(II) 1 mole of solvent as vapor at pressure  $p \rightarrow$  1 mole of solvent as vapor at pressure  $p^0$ .

$$F^0 - F = \Delta F = \int_p^{p^0} V dp = \int_p^{p^0} \frac{RT}{p} dp = RT \ln \frac{p^0}{p}$$

where  $F^0$  is the free energy of one mole of the vapor at pressure  $p^0$  and  $F$  is the free energy at pressure  $p$ .

This mole of solvent vapor is then added reversibly to the reservoir of pure solvent by applying an external pressure infinitesimally greater than  $p^0$ . The process may be written as (III).

(III) 1 mole solvent as vapor at vapor pressure  $p^0 \rightarrow$  1 mole solvent as liquid.

$$\Delta F = 0$$

All the steps are carried out isothermally and reversibly, and the total change of free energy involved in the transfer of 1 mole of solvent from solution to solvent is

$$\Delta F = RT \ln \frac{p^0}{p} \quad [24]$$

regardless of how the transfer is carried out.

This formula can be used equally well for transferring a mole of solvent from a solution of one concentration  $c$  having a vapor pressure  $p$  to a solution of another concentration  $c'$  having a vapor pressure  $p'$ . Thus

$$\Delta F = RT \ln \frac{p'}{p} \quad [25]$$

Moreover, these formulas are not limited to the solvent. They may be applied to any volatile material in the solution whether called solvent or solute.

In ideal solutions where the vapor pressure of the volatile component is proportional to the mole fraction  $N$ , the equation is written thus:

$$\Delta F = RT \ln \frac{N'}{N} \quad [26]$$

In very dilute solutions where Raoult's law applies, the vapor pressures are proportional to the concentration of the solute; thus

$$\Delta F = RT \ln \frac{c'}{c} \quad [27]$$

*Example 7.* What is the free energy of dilution involved when one mole of solute in a 0.01 molal aqueous solution at 25° is mixed with enough water to give a 0.001 molal solution?

$$\Delta F = RT \ln \frac{c'}{c} = 1.987 \times 298.1 \times 2.303 \times \log \frac{0.001}{0.01} = -1364 \text{ cal.}$$

The negative sign indicates that the process of dilution is spontaneous. The reverse process in which the solute becomes more concentrated would not occur spontaneously as explained on page 138.  $\Delta F$  would have a positive sign.

It has been shown that the four properties, vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure, may be readily calculated for dilute solutions, but that the simple formulas fail when applied to concentrated solutions. It is a necessary consequence of thermodynamics, however, that at a given temperature the deviations from ideal solutions are the same in all the different properties. For example, if the vapor-pressure lowering is known, the osmotic pressure may be calculated with exactness, even in concentrated solutions where Raoult's law does not hold and where the osmotic pressure cannot be calculated from the gas laws. These relations follow from the fact that the free energy of dilution is the same no matter whether it is effected by evaporation, by freezing, or by application of pressure through a semi-permeable membrane.

The free energy of transfer of a mole of solvent from solution to solvent is given by equation (24). The transfer of solvent may be effected also by osmosis. A large quantity of the solution is placed in a cylinder provided with a movable semi-permeable membrane for a piston, and the pressure is slowly increased from atmospheric pressure to  $P + 1$ , where  $P$  is the osmotic pressure. The free energy change for this step is obtained by integration of equation (23); if the liquid is incompressible we have

$$\Delta F = \int_1^{P+1} v_1 dp = v_1 P$$

where  $v_1$  is the volume of the solution. Then the pressure is increased infinitesimally, and solvent passes through the semi-permeable membrane, because extra pressure on the solution is slightly greater than the osmotic pressure  $P$ . The free energy change is zero since this is an isothermal, reversible process in which the pressure on each phase is kept constant. After 1 mole of solvent has been forced out,\* it is taken from the cylinder, and the pressure on the remaining volume of solution,  $v_2$ , is slowly reduced to one atmosphere.

$$\Delta F = -v_2 P$$

The total change in free energy is

$$\Delta F = (v_1 - v_2)P = V'P \quad [28]$$

\* It is assumed here that the molecular weight is the same in the liquid and gaseous states. If it is not, sufficient liquid is removed to produce 1 mole of vapor.

where  $V' = v_1 - v_2$  is the volume change when 1 mole of solvent is added to a large quantity of the solution at constant temperature and pressure.  $V'$  is sometimes called the partial molar volume of the solvent in the solution (page 533); it is very nearly equal to the volume of 1 mole of the pure solvent.

Combining equations (24) and (28),

$$PV' = RT \ln \frac{p^0}{p} \quad [29]$$

$$P = \frac{RT}{V'} \ln \frac{p^0}{p} \quad [30]$$

With this formula it is possible to calculate the osmotic pressure of a solution from the vapor pressures of the solvent and the solution, and the molar volume of the solvent. At high concentrations, where the osmotic pressures calculated by the simple gas law (equation 22) are in error by more than 30 per cent, the values calculated by equation (30) check with the observed values within less than 1 per cent.

*Example 8.* Calculate the osmotic pressure of a 1*M* sucrose solution in water from the fact that at 30° the vapor pressure of the solution is 31.207 mm. The vapor pressure of water at 30° is 31.824 mm. The density of pure water is 0.99564.

$$\begin{aligned} P &= \frac{RT}{V'} \ln \frac{P_0}{P} \\ V' &= \frac{18.02}{0.99564} = 18.10 \\ P &= \frac{82.054 \times 2.303}{18.10} \left( \log_{10} \frac{31.824}{31.207} \right) \times 303.1 \\ &= 26.93 \text{ atm.} \end{aligned}$$

Equation (30) can be used also for deriving formula (22). For ideal solutions or dilute solutions, where Raoult's law holds,

$$p = p^0 N_1$$

where  $N_1$  is the mole fraction of the solvent, and

$$\ln \frac{p^0}{p} = -\ln N_1 \quad [31]$$

Since  $N_1$  is equal to  $1 - N_2$ , where  $N_2$  is the mole fraction of the solute,

$$\ln N_1 = \ln (1 - N_2) \quad [32]$$

Then substituting into equation (30)

$$P = \frac{RT}{V'} [-\ln (1 - N_2)] \quad [33]$$

Expanding in a series

$$P = \frac{RT}{V'} (N_2 + \frac{1}{2}N_2^2 + \frac{1}{6}N_2^3 + \dots) \quad [34]$$

When  $N_2$  is small, higher powers may be neglected and

$$PV' = N_2 RT \quad [35]$$

But  $N_2 = n_2/(n_1 + n_2)$ , and in dilute solutions  $N_2 = n_2/n_1$ , where  $n_2$  is the number of moles of solute and  $n_1$  the number of moles of solvent. Therefore,

$$PV'n_1 = n_2 RT \quad [36]$$

Setting  $v$ , the volume of the dilute solution containing  $n_2$  moles of solute equal to  $V'n_1$  (i.e., to the volume of 1 mole of solvent  $\times$  the number of moles of solvent)

$$Pv = n_2 RT \quad [37]$$

This is equivalent to (22), discovered experimentally, and it is evident from the approximations introduced why it cannot hold for concentrated solutions.

**Dissociation of Solutes.** If the solute is broken down into smaller units in solution, the effect on the vapor pressure and other related properties will be increased. Van't Hoff pointed out that the osmotic pressures of aqueous solutions of most salts and of all strong acids and bases are much greater than would be expected from the osmotic pressures of solutions of substances like cane sugar or urea for corresponding concentrations, and he showed that the fundamental equation,  $Pv = RT$ , would still hold, provided that an empirical factor,  $i$ , were introduced giving

$$Pv = iRT \quad [38]$$

It was originally believed that the factor  $i$  was a constant, but subsequently Arrhenius showed that it increases as the concentration diminishes. If the osmotic pressure of some substance, like cane sugar, which behaves normally, is represented by  $P_0$ , the factor  $i$  can be calculated by means of the expression

$$i = \frac{P}{P_0}$$

where  $P$  is the osmotic pressure of an abnormal solute at the same concentration. Since in dilute solution the osmotic pressure of a solution is proportional to the relative lowering of its vapor pressure  $\Delta p$ , to the elevation of its boiling point  $\Delta T_b$ , and to the lowering of its freezing point  $\Delta T_f$ , it follows that any one of these properties may be similarly employed to calculate the value of the empirical factor  $i$ . Thus

$$i = \frac{P}{P_0} = \frac{\Delta p}{(\Delta p)_0} = \frac{\Delta T_f}{(\Delta T_f)_0} = \frac{\Delta T_b}{(\Delta T_b)_0} \quad [39]$$

where the subscript zero refers to the solution of a normal solute. The vapor-pressure lowering,  $\Delta p$ , is equal to  $p_{\text{solvent}} - p_{\text{solution}}$ .

The abnormal behavior of salts is shown in Table V, which gives the values of the molal freezing-point depressions  $\Delta T_f/m$  of typical salts together with the corresponding value of  $i$  at several different concentrations. Since for a normal solute  $\frac{\Delta T_f}{m}$  is 1.86,  $i = \frac{\Delta T_f}{m} / 1.86$ .

TABLE V

VALUES OF MOLAL FREEZING-POINT DEPRESSIONS<sup>1</sup>

Molality ( $m$ )		0 005	0 006	0 01	0 02	0 05	0 1	0 2	0 5
KCl	$\Delta T_f/m$	3 64	3 64	3 61	3 56	3 50	3.45	3 39	3 31
	$i$	1 96	1 95	1 94	1 91	1 88	1 86	1 83	1 80
K <sub>2</sub> SO <sub>4</sub>	$\Delta T_f/m$	5 30	5 28	5 19	5 04	4 77	4 56	4 32	3 94
	$i$	2 85	2 84	2 79	2 71	2 57	2 45	2 33	2 12
MgSO <sub>4</sub>	$\Delta T_f/m$	3.14	3.11	3 00	2 85	2.63	2.46	2 27	2 00
	$i$	1 69	1.67	1 61	1 53	1 42	1 32	1 22	1 03
K <sub>3</sub> Fe(CN) <sub>6</sub>	$\Delta T_f/m$	6 84	6.81	6 69	6.19	5.60	5 30	5 00	4 55
	$i$	3 68	3.66	3.60	3 33	3 02	2.86	2.70	2.45

<sup>1</sup> Noyes and Falk, *J. Am. Chem. Soc.*, **32**, 1011 (1910).

The data are shown graphically in Fig. 69 where it is seen that  $i$  approaches the values 2, 3 and 4 at infinite dilution. It is evident that the depressions are considerably greater than those of normal solutes such as cane sugar or mannitol. For a given solute they increase as the concentration is decreased and, at infinite dilution, approach definite limits which are multiples of the normal depression 1.86°. Thus, with solutions of KCl and MgSO<sub>4</sub>, the molal depression approaches the value 3.72° (or  $2 \times 1.86^\circ$ ) as the solutions are diluted, while the respective limits toward which the molal depressions of solutions of K<sub>2</sub>SO<sub>4</sub> and K<sub>3</sub>Fe(CN)<sub>6</sub> tend are  $3 \times 1.86^\circ$  and  $4 \times 1.86^\circ$ .

These facts together with numerous other properties of dilute solutions of acids, bases, and salts find their most satisfactory explanation in the theory of electrolytic dissociation.

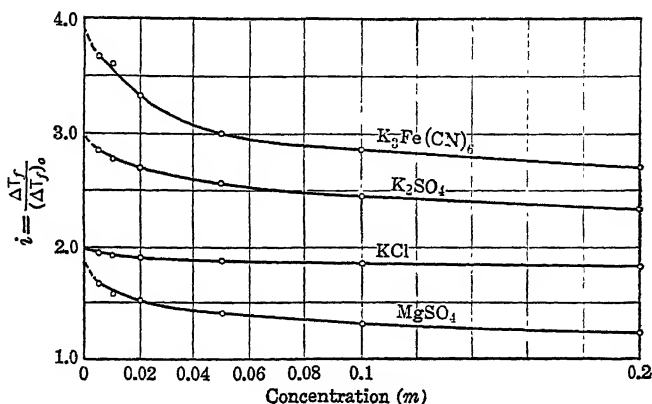


FIG. 69

**Arrhenius' Theory of Electrolytic Dissociation.** In 1887, Arrhenius\* proposed the theory that aqueous solutions of acids, bases, and salts are dissociated, to a greater or less extent, into positively and negatively charged particles or *ions*, and that the increase in the number of dissolved units due to this dissociation is the cause of the enhanced osmotic pressure. He strengthened this theory greatly by pointing out that substances which give abnormal osmotic effects yield solutions which conduct the electric current, whereas solutions of such substances as cane sugar, urea, and alcohol, which exert normal osmotic pressures, do not conduct electricity any better than the pure solvent. In other words, only electrolytes† are capable of undergoing ionic dissociation; hence Arrhenius termed the hypothesis the *electrolytic dissociation theory*. When charged electrodes are introduced into the solution, the positive ions move toward the negative electrode and the negative ions move toward the positive electrode, the passage of a current through the solution consisting in the transfer of electric charges. The relation between electrical conductance and the degree of ionization will be discussed on page 473.

The chemical properties of an ion are very different from the properties of the corresponding atom or molecule. For example, sodium

\* Arrhenius, *Z. physik. Chem.*, 1, 631 (1887).

† The term *electrolyte* strictly refers to the solution of an ionized substance, although it is often applied to acids, bases, or salts, because, when dissolved, they produce electrolytes.



ions are stable in an aqueous solution of sodium chloride, whereas sodium atoms in the electrically neutral condition react violently with water, evolving hydrogen and forming a solution of sodium hydroxide. Chlorine in such compounds as  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , etc., is not precipitated by silver nitrate, since these compounds are not dissociated by water. Also chlorine may be present in a compound which is dissociated by water and yet not exhibit its characteristic reactions because it is present in a complex ion. For example in chlorate ion,  $\text{ClO}_3^-$ , it is not precipitated by silver nitrate.

Arrhenius pointed out further that the multiples of the normal freezing-point depression at infinite dilution, such as are shown in Fig. 68 are identical with the number of ions into which a molecule of solute can dissociate. Thus  $\text{KCl}$  can dissociate into two ions,  $\text{K}^+$  and  $\text{Cl}^-$ , and at infinite dilution the depression is just twice the normal value. In other words,  $i$  is 2. For  $\text{K}_2\text{SO}_4$  three ions are possible,  $2\text{K}^+$  and  $\text{SO}_4^{=}$ ; thus  $i$  has a value of 3 at infinite dilution. Likewise  $\text{MgSO}_4$  gives two ions, and  $\text{K}_3\text{Fe}(\text{CN})_6$  gives four ions,  $3\text{K}^+$  and  $\text{Fe}(\text{CN})_6^{=}$ . This explanation of Arrhenius has been abundantly verified.

*Example 9.* The freezing point of a 0.01 molal solution of barium chloride is  $-0.050^\circ$ . What is the approximate vapor pressure of the solution at  $25^\circ$  if the vapor pressure of pure water is 23.756 mm.?

$$N_2 = \frac{0.01}{1000/18.02} = 1.80 \times 10^{-4}$$

$$i = \frac{0.050}{0.01 \times 1.86} = \frac{\Delta p}{1.80 \times 10^{-4} \times 23.756}$$

$$\Delta p = 0.0115 \text{ mm.}$$

$$p = 23.756 - 0.0115 = 23.744 \text{ mm.}$$

Further discussion of the constant  $i$  and the influence of concentration on the behavior of electrolytes will be deferred until page 501.

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## PROBLEMS

1. The vapor pressure of a solution containing 13 g. of solute in 100 g. of  $H_2O$  at  $28^\circ$  is 27.371 mm. Calculate the molecular weight of the solute. The vapor pressure of water at this temperature is 28.065 mm. *Ans.* 92.3.

2. If 68.4 g. of sugar (molecular weight = 342) is dissolved in 1000 g. of water, what are (a) the vapor pressure, and (b) the osmotic pressure, at  $20^\circ$ ? (c) What is the freezing point? (d) What is the boiling point? The density of the solution at  $20^\circ$  is 1.024. The vapor pressure of water at  $20^\circ$  is 17.363. The heat of vaporization of water is 539 cal. per g., and the heat of fusion is 79.6 cal. per g.

*Ans.* (a) 17.30 mm. (b) 4.61 atm. (c)  $-0.372^\circ$ . (d)  $100.103^\circ$ .

3. Solutions of hydrogen chloride in chlorobenzene obey Henry's law. In dilute solutions

$$K = \frac{p \text{ (in atmospheres)}}{m \text{ (in moles, 1000 g. solvent)}} = 4.38.$$

What is the partial pressure in millimeters of Hg of hydrochloric acid over a 1 per cent by weight solution of HCl in chlorobenzene? *Ans.* 92.3.

4. An aqueous solution of maltose at  $25^\circ$  has a vapor pressure of 23.476 mm whereas pure water has a vapor pressure of 23.756 mm. What is the osmotic pressure of the solution? *Ans.* 16.11 atm.

5. When cells of the skeletal muscle of a frog were placed in a series of sodium chloride solutions of different concentrations, it was observed microscopically that the cells remained unchanged in 0.7 per cent NaCl solution but shrank in more concentrated solutions and swelled in more dilute solutions. Calculate the osmotic pressure of the cell protoplasm at  $25^\circ$ . *Ans.* 5.91 atm.

6. Calculate  $\Delta F$  for the mixing of 1 mole of benzene and 1 mole of toluene, to give an ideal solution at  $25^\circ$ . *Ans.*  $-822$  cal.

7. An 0.1  $M$  solution of a substance in water is prepared. At  $25^\circ$  the substance is 26 per cent dissociated into two molecules. Calculate the osmotic pressure at this temperature. *Ans.* 3.08 atm.

8. Calculate the vapor pressure of a 15 per cent solution of glucose at  $20^\circ$ . The vapor pressure of water at this temperature is 17.363 mm.

9. Ten grams of benzene, 10 g. of toluene, and 10 g. of naphthalene are added together to give a homogenous solution. Assuming that the solution is ideal, how many grams of toluene will be vaporized by passing through 10 liters of air at  $30^\circ$  if the vapor pressure of toluene at this temperature is 36.7 mm. and that of benzene is 118.5 mm.?

10. (a) If 10 g. of phenol added to a given quantity of benzene lowers the freezing point of benzene  $X$  degrees, how many degrees (in terms of  $X$ ) will 20 g. lower it?

(b) The boiling point of a certain solvent is  $B^\circ$  and the boiling point of a solution of this solvent containing 10 per cent by weight of a nonvolatile solute is  $B + Y^\circ$ . Calculate in terms of  $B$  and  $Y$  the boiling point of a solution containing 20 per cent by weight of the solute, assuming an ideal solution.

11. Calculate the freezing-point depression of water produced by dissolved air in equilibrium with air (79 per cent nitrogen, 21 per cent oxygen) at 1 atm. At  $0^\circ$ , 100 g. of water dissolves 4.49 ml. of oxygen and 2.35 ml. of nitrogen when the pressure of each gas is 1 atm.

12. Calculate the melting point of solution of 20 g. of naphthalene in 80 g. of heptachloropropane.

13. When 1.4511 g. of dichloroacetic acid is dissolved in 56.8699 g. of carbon tetrachloride the boiling point is increased  $0.518^{\circ}$ . The boiling point of carbon tetrachloride is  $76.75^{\circ}$ , and its heat of vaporization is 46.5 cal. per g. at the boiling point. What is the molecular weight of the acid? How can the discrepancy be explained?

14. Calculate the change in free energy involved when a mole of water is transferred (by isothermal distillation) at  $25^{\circ}$  from pure water to a large quantity of a 9.9 per cent glycerol solution which has a vapor pressure of water amounting to 23.300 mm. The vapor pressure of pure water is 23.756 mm.

15. Human blood freezes at  $-0.56^{\circ}$ . What is its osmotic pressure at  $37^{\circ}$ ?

16. A certain number of grams of a given substance in 100 g. of benzene lowers the freezing point by  $1.28^{\circ}$ . The same weight of solute in 100 g. of water gives a freezing point of  $-1.395$ . If the substance has its normal molecular weight in benzene and is completely dissociated in water, into how many ions does a molecule of this substance dissociate when placed in water?

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17. The vapor pressure of water at  $25^{\circ}$  is 23.756 mm. Calculate the vapor pressure of solutions containing (a) 6.01 g. of urea, (b) 0.94 g. of phenol, and (c) 6.01 g. of urea + 0.94 g. of phenol per 1000 g. of water, assuming no chemical action between the two substances. (d) Calculate (c) assuming that a stable compound is formed containing 1 molecule of urea to 1 molecule of phenol.

18. Using in part data from an earlier chapter, calculate the boiling point of a solution containing 10 g. of heptachloropropane in 100 g. of carbon tetrachloride, assuming that the heptachloropropane is nonvolatile.

19. How many grams of methanol must be added to a 10-liter tank of water to prevent freezing at  $-10^{\circ}$ ? How many grams of calcium chloride  $\text{CaCl}_2$ , assuming complete dissociation and no interaction?

20. Ten grams of benzene vaporizes isothermally from a solution containing an equimolecular mixture of benzene and diphenyl and condenses in a large amount of solution of benzene and nitrobenzene in which the mole fraction of benzene is 0.1. Calculate the change in free energy, assuming that both solutions are ideal.

21. (a) What molal concentration of solutes at  $20^{\circ}$  is required to raise a column of solution having a density of approximately 1.0 to a height of 300 ft.?<sup>\*</sup>

(b) What is the vapor pressure of the solution at  $20^{\circ}$ ? The vapor pressure of pure water at  $20^{\circ}$  is 17.363.

22. The total vapor pressure of a solution containing 3 per cent by weight of  $\text{C}_2\text{H}_5\text{OH}$  in water is 760 mm. at  $97.11^{\circ}$ . The vapor pressure of pure water at this temperature is 685 mm. Using Raoult's law and Henry's law, calculate the partial pressure at  $97.11^{\circ}$  of ethanol and water over a solution containing 0.02 mole fraction of ethanol.

---

23. Purified nitrogen gas is slowly bubbled through a solution of 3.000 g. of a nonvolatile organic compound dissolved in 200 g. of benzene and then bubbled through pure benzene. The solution is found to be 2.1540 g. lighter, while the pure benzene suffered a loss in weight of 0.0160 g. What is the apparent molecular weight of the dissolved substance?

<sup>\*</sup> The circulation of sap in a tall redwood tree is not to be attributed *entirely* to osmosis.

24. By combining Raoult's law, the Clausius-Clapeyron equation, and Trouton's rule, show that the boiling point  $T_B$  of a dilute solution of a nonvolatile solute and the mole fraction of *solvent*  $N_A$  are related by the approximate equation

$$N_A T_B^{21/R} = \text{constant}$$

25. Derive an equation which relates the elevation in the boiling point of a liquid by the addition of a nonvolatile solute to the corresponding lowering of the vapor pressure.

## CHAPTER XI

### COLLOIDS

**Definitions.** In the course of his investigations on diffusion in solutions, Thomas Graham\* drew a distinction between crystalline solutes and certain amorphous solutes such as starch, albumin, and caramel which diffuse much more slowly. To this latter type of substance he gave the name *colloid* (κόλλα, *glue*, and εἶδος, *form*). These colloids give solutions which have very low osmotic pressures and freezing points which are nearly the same as those of the pure solvent. The term colloid, as now used, applies not so much to a class of material as to a state of subdivision.

If the particles of a substance are reduced in size until the dimensions become submicroscopic and distributed throughout a second substance, the resulting system is called a *disperse system*. The particles are called *dispersoids*, and the suspending liquid, gas, or solid is called the *dispersing medium*. The characteristic properties of disperse systems are attributable to the enormous surface of the dispersed phase. If a cube of any substance 1 cm. on an edge, having a total surface of 6 sq. cm., is cut in half in the three directions, there will be 8 cubes having edges of 0.5 cm. and the surface will be  $8 \times 6 \times 0.5^2$  or 12 sq. cm. If cut into 1000 cubes 1 mm. on an edge, the total surface will be 60 sq. cm. If the cubes are  $1\mu$ † on an edge, the surface area will be increased to 60,000 sq. cm., or 6 sq. m. If the cubes are  $0.001\mu$  on an edge there will be  $10^{21}$  cubes, and the area will be 6000 sq. m. or  $1\frac{1}{2}$  acres. It is obvious that surface effects which are undetected on material having an area of 6 sq. cm. may become very pronounced when the material is dispersed to give a total surface of several square meters.

One of the most important results of this large surface is the adsorption of ions and other materials by the particles. This adsorption may lead to the formation of electrical charges around the particles which prevent them from collecting into large aggregates.

If the particles are large they can be seen with the naked eye and they have essentially the properties of ordinary material, whereas

\* Graham, *Trans. Roy. Soc. (London)* **151**, 183 (1861).

† The symbol  $\mu$  refers to a micron which is  $10^{-6}$  m. or  $10^{-4}$  cm.

if they are very small they are indistinguishable from true solutions. Between these two regions is the colloidal state, in which the particles are small enough to have great surface area but large enough so that the solution is not strictly homogeneous and the presence of discrete particles can be detected with the ultramicroscope. The size of the dispersed particles determines whether or not a system is to be considered as colloidal. It is arbitrarily considered that particles with diameters between  $0.001\mu$  and  $1\mu$  ( $10^{-7}$  and  $10^{-4}$  cm.) are colloids, although there is no sharp distinction at these extremes. Particles larger than  $1\mu$  may be regarded as ordinary matter, and particles less than  $0.001\mu$  are usually regarded as constituting true solutions. Dust particles may have a diameter of  $10^{-4}$  cm., and hemoglobin or egg albumin or certain particles of colloidal gold have diameters of about  $10^{-7}$  cm.

Colloids are conveniently classed as *lyophilic* colloids when the dispersion medium exerts a dissolving or attractive influence on the dispersed phase; and as *lyophobic* colloids when there is very little attraction between the particles and the liquid in which they are suspended.

**Preparation of Colloids.** Colloids may be produced by *dispersion methods* in which relatively coarse material is divided into fine particles of colloidal dimensions. They are used particularly in the preparation of emulsions. Liquids may be dispersed in gases by a properly directed stream of gas sweeping across a constantly renewed liquid surface as in an atomizer. A liquid may sometimes be dispersed in a second liquid, in which it is insoluble, by merely shaking the two liquids together. The resulting *emulsion* consists of small droplets of the first liquid  $10^{-7}$  —  $10^{-4}$  cm. in diameter suspended throughout the second liquid. An emulsifying agent, such as soap, is usually added to aid in the formation of the emulsion. Liquids or solids can be effectively dispersed in liquids by means of the *colloid mill*.<sup>\*</sup> Large drops or coarse particles are suspended in water or other liquid and exposed to a powerful shearing force in the mill by passing the material between two accurately machined disks which rotate in opposite directions at a very high velocity while nearly touching each other.

Colloids are more often prepared by *condensation methods* in which the molecules or small aggregates are gathered together into larger aggregates. This procedure is thermodynamically spontaneous for it involves a decrease in area and surface free energy of the system. Condensation methods may be illustrated by the formation of pre-

<sup>\*</sup> Travis, "Mechanochemistry and the Colloid Mill," Chemical Catalog Co., New York, 1928.

precipitates in solution or by the cooling of water vapor to give a fog. Metals may be produced in the colloidal state by vaporizing them with an electric arc and condensing under water. This method was

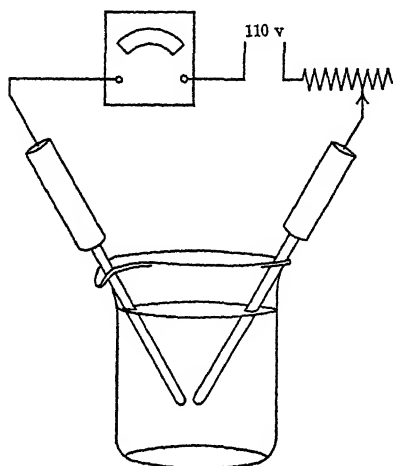


FIG. 70

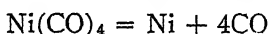
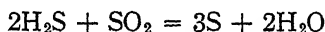
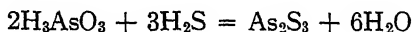
devised in 1897 by Bredig, and the simple apparatus for producing colloids by his arc method is shown in Fig. 70. A rheostat, arranged to give a current of 5 to 10 amperes, is connected to an ordinary 110-volt circuit, the wires are brought in contact for an instant under cold water, and then they are drawn apart quickly to a distance of 2 or 3 mm., thus forming an arc. Clouds of metal are vaporized and immediately condensed. Larger portions of the wire are torn off, and they settle as a coarse suspension. A trace of potassium hydroxide in the water helps to stabilize the colloid. Bredig prepared

colloidal solutions of gold, platinum, silver, and other metals. A deep red colloidal gold solution contained as much as 14 mg. of gold in 100 ml. of water. Somewhat better results are obtained by surrounding the arc with a housing which prevents the liquid from actually touching the ends of the wires. Spectrograms show that very little of the liquid is decomposed if the arc is protected.

By means of a high-frequency arc, Svedberg and his co-workers have succeeded in preparing colloids of most of the metals, including those of the alkalis. Ether, free from water and oxygen, may be employed as the dispersion medium.

Lyophobic colloids are often produced by precipitation reactions if the concentration of electrolytes is kept low. If there is a high concentration of ions the colloidal particles are likely to form large particles and settle out as will be described later.

The following reactions in which electrolytes are not produced illustrate the formation of colloids by direct chemical precipitation.



In the first reaction, if arsenious chloride is used in place of the arsenious oxide, hydrochloric acid will be produced in the reaction instead of water, and the arsenious sulfide will be partly coagulated by the ions produced.

Even when electrolytes are produced, it is possible to obtain the precipitate in the colloidal state if the solutions are dilute. The formation of colloidal ferric oxide by hydrolysis of ferric chloride, the production of colloidal gold by reduction of auric chloride with reducing agents such as tannic acid or formaldehyde, and precipitation of colloidal barium sulfate or silver chloride or silicic acid are examples of this common method of preparing colloids. Sometimes it is necessary to remove the electrolytes from the colloidal solution by techniques which are described in the following sections.

Material in solution may sometimes be thrown out in the colloidal state by mixing with a second solvent in which the material is less soluble. For example, sulfur dissolved in alcohol is obtained as a white milky colloid solution when poured into an excess of water.

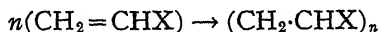
The classical methods for preparing colloids which have just been described refer chiefly to the lyophobic colloids. The lyophilic colloids are perhaps of more general importance, particularly in the fields of biology and industrial chemistry. Resins are natural or artificial mixtures of organic nature formed by such reactions. They are liquid, soft or fusible, or have passed through such a state in preparation. In the early stages of their formation, they will dissolve in organic solvents and separate out in films when the solvent is evaporated. They are usually amorphous and sometimes possess a glassy nature. Rubber, the asphalts, the cellulose derivatives, and the synthetic and natural resins are formed in reactions of this general type. Natural resins are excreted from plants; shellac, from animal organisms.

The production of lyophilic colloids often involves a process of solution or dispersion in which the solvent overcomes the attractive force between molecules which is produced by dipole-dipole interaction. Nitrocellulose for example is dissolved by acetone or by a mixture of ether and alcohol giving collodion, and the colloidal properties of the system are retained after the solvent has been evaporated and a gel is formed. Rubber dissolved in carbon tetrachloride, starch in aqueous solutions of zinc chloride for use in dry batteries, casein taken up in dilute acid or alkali solutions are all examples of lyophilic colloids. The non-aqueous colloidal systems are becoming increasingly important with the extensive use of lacquers such as, for example, a



polymer of phthalic anhydride and glycerine dissolved in an organic solvent such as acetone or dioxane.

The polymerization reactions in which molecules react chemically to form larger aggregates are particularly important. Several of these have been studied in detail,\* including the polymerization of the hydroxy acids, and the ethylene derivatives which may react as follows:



where X is a group such as  $\text{C}_6\text{H}_5$ , OH, Cl or  $\text{OCH}_3$ . The polystyrenes produced from  $\text{H}_2\text{C}=\text{CHC}_6\text{H}_5$  constitute a specific example. Some of these polymerization reactions can be studied as they proceed by the increasing molecular weights of the particles and by the increasing viscosity.

The separation of proteins and other colloids into different fractions can be brought about by changing the solvent, the salt concentration, or the temperature.†

**Purification of Colloids.** The marked difference between the rate of diffusion of crystalline material and colloids renders their separation comparatively easy. If a solution containing both crystalline material and colloids is separated from pure water by a colloidal membrane, such as parchment, the crystalloids will pass through the membrane and the colloids will be left behind. This process was termed *dialysis* by Graham, and the apparatus employed to effect such a separation is called a *dialyzer*. When a solution of sodium silicate is added to an excess of hydrochloric acid and placed in a dialyzer, the resulting sodium chloride and the hydrochloric acid diffuse away, leaving colloidal silicic acid.

Various natural and artificial membranes may be used for dialysis; Visking sausage casings of cellulose acetate are widely used, or sacks of thin collodion may easily be prepared. These membranes contain small pores which provide continuous channels for the solution, through which dissolved molecules and ions can diffuse, but through which the large colloid particles cannot diffuse. Dialysis may be regarded as a process of fractional diffusion; it is not to be confused with osmosis in which nothing but solvent can pass through the semi-permeable membrane. The rate of dialysis depends on many factors — the area of the dialyzer, the size of the pores, the temperature, the electrical charges, and the relative concentration of solution on the two

\* Carothers, *Chem. Rev.*, **18**, 367 (1931).

Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936); **61**, 3334 (1939).

† Cohn, *et al.*, *J. Am. Chem. Soc.*, **62**, 3386, 3396 (1940).

sides of the membrane. In practical work, fresh water is passed around the dialyzing sack to expedite the separation. Sometimes the solution is heated.

Many colloids are prepared under conditions where an excess of ions is present, and they are rendered more stable by dialysis. It is possible, however, to remove too many ions and cause coagulation. The ions may be removed also by inserting electrodes on each side of the membrane and passing a current of electricity through the solution. This process is called *electrodialysis*.

In the process of ultrafiltration the liquid medium as well as the material in true solution is removed from the colloidal material. Pressure is applied to the solution in a strong cylinder so as to force the liquid through the very small holes of a special membrane. A tank of compressed gas offers a convenient source of pressure. Filter papers may be used for ultrafiltration by impregnating them with solutions of collodion in acetic acid. Graded filters of different effective pore size can be made by changing the concentration of the acid.\* Ultrafiltration is a complex process, involving electrical attraction and adsorption by the filter as well as the ordinary process of mechanical separation. For example, if we attempt to filter a ferric hydroxide colloid the filter becomes negatively charged in contact with the water, and on the entrance of the positively charged particles into the pores of the filter the colloid is discharged and the colloidal ferric hydroxide is precipitated. After the pores of the filter become partly stopped with particles of the colloid, the colloidal solution or *sol* will then pass through very slowly.

Ultrafilters are useful in removing impurities from sols, and they find extensive application in bacteriology. Bacteria can generally be removed from solutions by ultrafilters, but certain diseases such as the common cold are connected with "filterable viruses" which pass through the finest ultrafilters.

**Optical Behavior.** When a narrow beam of sunlight is admitted into a darkened room, the dust particles in its path are rendered visible by the scattering of the light at the surface of the particles. If the air of the room is free from dust, no shining particles will be seen and the space is said to be "optically void." If the particles of dust are very minute, the beam of light acquires a bluish tint.

The luminosity of the path of a beam of light is known as the *Tyndall effect* and may be considered as an indication of the presence of suspended particles, provided the luminosity is not caused by fluores-

\* Ferry, "Ultrafilter Membranes and Ultrafiltration," *Chem. Rev.*, **18**, 373-455 (1937).

cence. Almost all colloid solutions exhibit this phenomenon when a powerful beam of light is passed through them, thus proving the presence of discrete particles in the solutions.

Great advances in colloid chemistry came with the invention of the ultramicroscope in 1903 by Siedentopf and Zsigmondy. With this instrument the motions of the colloid particles became visible, and Brownian movement was then proved to be a necessary accompaniment of all colloidal systems. In an ultramicroscope a powerful beam of light is brought to a focus within the colloidal solution, and this image is viewed through a standard microscope, the axis of which is at right angles to the path of the beam. When examined in this way a colloid solution usually appears to be swarming with minute particles moving rapidly in a dark field, whereas a true solution if properly prepared appears optically void.

It is necessary to view the particles by reflected light rather than by transmitted light because the colloidal particles are smaller than the wavelength of visible light. The intensity of the light rather than the magnifying power of the microscope is the limiting factor in detecting the smallest colloid particles with the ultramicroscope. It is possible to extend the lower limit of detection by using shorter wavelengths, i.e., ultraviolet light, with quartz lenses and photographic plates. It should be emphasized that the apparent size of the bright image bears no relation to the size of the particle. It is possible, however, to count the number of particles in a given volume. By means of a chemical analysis, the mass of colloid per unit of volume can be determined, and from this, the average mass of each particle can be calculated.

*Example 1.* In the field of an ultramicroscope, 20 particles of colloidal mercury were observed. This field, approximately 0.02 mm. wide, comprised a volume of  $1 \times 10^{-9}$  ml. A liter of this colloidal mercury solution was stirred rapidly with a gold stirrer until all the mercury was removed. The increase in weight of the stirrer was 8 mg. because the mercury amalgamated on it. Assuming that the particles of mercury were spherical and that they had a density of 13.5, calculate the average radius of the colloidal particles.

$$20 \times \frac{1 \times 10^3}{1 \times 10^{-9}} = 2 \times 10^{13} \text{ particles per liter}$$

$$0.008 = 2 \times 10^{13} \times \frac{4}{3} \times 3.14 \times r^3 \times 13.5$$

$$r = 1.9 \times 10^{-6} = 190 \text{ \AA.}$$

These small colloid particles can be seen with the ultramicroscope only if their refractive index differs from that of the medium in which they are suspended. With metallic colloids this difference is large and

excellent definition is obtained, making possible the detection of particles as small as  $0.004\mu$  or  $40 \text{ \AA}$ . in diameter. The marked difference in the behavior of lyophobic and lyophilic colloids is brought out again. The lyophilic colloids are partly combined with the solvent and accordingly it is much more difficult to see lyophilic colloids than lyophobic colloids in the ultramicroscope even if they are fairly large.

By using ultraviolet light having a wavelength shorter than that of visible light it is possible to photograph smaller colloids than can be seen with the microscope.

A new instrument, the electron microscope, is now available for examining much smaller particles. The principle of the electron microscope depends on the fact that a beam of electrons under a constant voltage has the properties of a beam of light. At the voltages used the wavelength corresponds to  $0.05 \text{ \AA}$ . and it is clear why particles which are smaller than the wavelength of visible light  $4000$  to  $8000 \text{ \AA}$ ., may still be seen in good detail with the electron microscope. Practical difficulties limit the utilization of the full theoretical resolving power of the electron microscope but photographs with good detail can be obtained with a magnification of more than  $10,000$  times.

The electron microscope is provided with a series of electrostatic and electromagnetic fields which focus the electron beam just as glass lenses focus ordinary light. The voltage and current must be closely controlled. The specimen to be studied is placed on a very thin collodion film and a focused beam of electrons is passed through. Where the material is denser, more of the electrons are scattered but where the material is thin, the electrons continue on their course and are focused on a fluorescent screen or a photographic plate.

The electron microscope has been developed only recently as a practical instrument but already interesting facts have been discovered with it.

With it filterable viruses such as tobacco-mosaic virus have been pictured for the first time and they are found to be rod-shaped in agreement with indirect measurements based on diffusion. Moreover, structural features in the simplest bacteria have been brought out, and the size and shape characteristics of various powders such as paint pigments or abrasives have been established. The structure of soaps and tissues also has been revealed as shown for example in Fig. 71.\*

\* Figure 71 is taken with the permission of the authors from a publication by Marton, McBain, and Vold on curd fibers of sodium laurate published in *J. Am. Chem. Soc.*, **63**, 1990 (1941).

**Kinetic Behavior.** Very small particles suspended in a liquid can be seen under the microscope to be in a state of ceaseless, erratic motion. Colloid particles as seen in the ultramicroscope undergo this motion, but larger particles, such as an aqueous suspension of gamboge, also exhibit a slow movement.



FIG. 71

This phenomenon, which had frequently been observed, was first properly interpreted in 1827 by the English botanist, Robert Brown, while examining a suspension of pollen grains. It is commonly known as *Brownian motion*. Brown stated that "the movements arose neither from currents in the fluid nor from its gradual evaporation; but belonged to the particle itself."

It is now known that the movement is caused by the actual bombardment of the particles by the molecules of the suspending medium.

It constitutes a visual confirmation of the random kinetic motion which had been assumed for the molecules of a gas (or liquid or solid) at any temperature above absolute zero.

This kinetic behavior is responsible for many of the important phenomena of colloids. It is used for separating different colloids and for determining their sizes and shapes. The particle sizes can be determined not only by direct photographing with an electron microscope or by counting with an ultramicroscope as already described, but in several indirect ways including diffusions and sedimentations under gravity or centrifugal force. Measurements of osmotic pressure may be used also. These phenomena will now be discussed in more detail.

**Diffusion.** It is to be expected that material will diffuse from a region of higher concentration. The rate of this diffusion has been studied quantitatively and it has a number of applications in the study of colloids. The diffusion constant or specific diffusion rate  $D$  is defined as the number of moles which diffuse across a unit area in unit time under a concentration gradient of unity. It can be shown (appendix, page 666) that

$$D = \frac{RT}{Nf} \quad [1]$$

where  $f$  is the frictional force opposing a particle which is moving with a velocity of 1 cm. per second,  $N$  is Avogadro's number, and  $R$  is the gas constant.

According to Stokes' law this force is given by equation (2)

$$f = 6\pi\eta r \quad [2]$$

where  $r$  is the radius of the spherical particle and  $\eta$  is the coefficient of viscosity of the surrounding medium. This formula was derived for particles which are large compared to the solvent molecules, and strictly speaking it applies only to spherical molecules. Combining equations (1) and (2)

$$D = \frac{RT}{N6\pi\eta r} \quad [3]$$

This is a useful equation from which the diffusion rate can be determined from the radius of the particle and the viscosity of the medium; or the size of the particle can be calculated from the rate of the diffusion of the colloids. One of the applications of this equation is the calculation of the Avogadro number  $N$ .

The intimate relationship between Brownian movement and diffusion was shown for the first time by Einstein.\* The actual movements of individual colloidal particles are seen to be complex and erratic, just as the motions of molecules in a gas had been imagined.

In Fig. 72 each circle represents the position of an individual colloid particle at intervals of 30 seconds as it is seen under the ultramicroscope while it moves along a path from  $A$  to  $B$  and on to  $P$  and  $Q$ . The dotted lines give the displacements along the  $x$  axis. Then  $\Delta x$  is the difference between two successive displacements. For example, in going from  $A$  to  $B$ ,  $\Delta x$  is obtained by subtracting the second dotted line from the top one and  $\Delta x/\Delta t$  is equal to this distance divided by the 30-second time interval,  $\Delta t$ . Of course, there will be movement also along the  $z$  axis at right angles to the  $x$ - $y$  plane, but the displace-

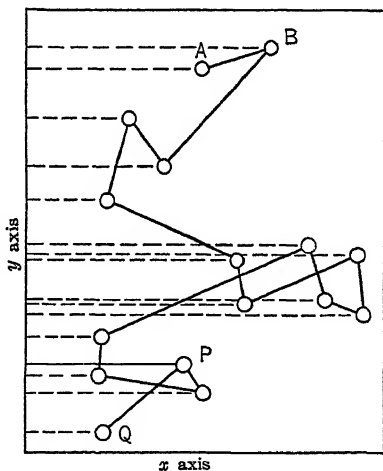


FIG. 72

\* Einstein, *Ann. Physik*, [4] 17, 549 (1905); 19, 371 (1906).

ments along any one axis are sufficient to calculate the diffusion rate or particle size.

The mean value of the square of the difference in the  $x$  displacements  $\overline{(\Delta x)^2}$  is related to the diffusion constant by Einstein's relation as follows,

$$\frac{\overline{(\Delta x)^2}}{\Delta t} = 2D \quad [4]$$

Then substituting in equation (3)

$$\overline{(\Delta x)^2} = \frac{RT}{N} \frac{\Delta t}{3\pi\eta r} \quad [5]$$

Perrin was probably the first to apply this formula to the measurement of individual particles, using suspensions of certain gums in water. He calculated the radius  $r$  by counting the particles obtained from a given weight of material, assuming that the particles were spherical. In this way he obtained an average value of  $6.8 \times 10^{23}$  for the Avogadro number  $N$ .

More accurate values for the Avogadro number have been obtained by Millikan and Fletcher,\* employing a minute drop of oil as the suspended particle. In the gaseous state, where the intermolecular distances are greater than in the liquid state, not only are the collisions less frequent but also the mean free paths are appreciably longer. These conditions are favorable to the study of the Brownian movement, and offer an opportunity for the determination of the Avogadro constant with a high degree of accuracy. As the mean of nearly six thousand measurements, Fletcher concluded that  $N = 6.03 \times 10^{23}$ .

This value is in perfect agreement with the values of the Avogadro number given on page 657, a fact which strengthens both the kinetic theory of gases and the assumption that these comparatively large particles behave as individual molecules in a gas.

The diffusion method has been used for determining the sizes of particles under different conditions. The rate of diffusion can be measured by a number of different methods—by direct chemical analysis of samples at different distances after definite time intervals, or by methods depending on the Tyndall effect or the absorption or refraction of light. Perhaps the simplest general method involves photographing a scale with fine divisions behind a boundary between a solution and the solvent. The distortion of the photograph of the scale permits a measurement of the blurring of the boundary. This in turn measures the rate at which the solute diffuses and changes the

\* Fletcher, *Phys. Rev.*, 4, 453 (1914).

refractive index. Great care must be exercised in eliminating mechanical vibrations and thermal inequalities.\*

Although equation (3) was derived only for spherical particles, it can be used in connection with certain other formulas if the shape factor occurs in both formulas in such a way as to cancel out. More recently the determinations of the diffusion constants has become important because they can be combined with measurements of sedimentation or viscosity to give the molecular weights of dissolved proteins or carbohydrates even when the shape of the colloid particle is unknown.†

**Viscosity.** Whereas the viscosity of a liquid is not markedly changed by the addition of a small amount of a lyophobic colloid such as colloidal gold in water, the viscosity of lyophobic colloidal solutions may become very great. The viscosity of high polymers, such as nitrocellulose, has long been used as a criterion for certain industrial operations, and now progress is being made in correlating viscosity with the size and shapes of the colloidal particles.

The particles may be spheres, rods, disks, or threads.

According to Staudinger,‡ the following formula holds for long-chain polymers which give threadlike particles

$$\frac{\eta - \eta_0}{\eta_0} = knc \quad [6]$$

where  $\eta$  is the viscosity of the solution,  $\eta_0$  is the viscosity of the solvent, and  $k$  is a constant for a given type of molecule;  $n$  is the number of units in the molecule ( $\text{CH}_2$  groups for example in a hydrocarbon) and  $c$  is the concentration of these units in solution. The constant  $k$  may be evaluated from measurements on materials of known molecular weight and then the number of units in another molecule, of the same type, can be calculated from measurements of viscosity. From these data the molecular weights can be calculated and in many cases they agree with the values found by other methods.§

**Osmotic Pressure.** The osmotic pressure or the lowering of the freezing point by colloids is exceedingly small but is nevertheless real. If the weight of a colloid particle multiplied by  $6.02 \times 10^{23}$  is regarded

\* Williams and Cady, "Molecular Diffusion in Solution," *Chem. Rev.*, **14**, 171 (1935).

† Svedberg and Pedersen, "The Ultracentrifuge," Oxford University Press, Oxford, 1940.

‡ Staudinger, "Die hochmolekularen organischen Verbindungen," Berlin, 1932; *Kolloid-Z.*, **82**, 129 (1938).

§ Mark, "Physical Chemistry of High Polymeric Systems," pages 258-293 Interscience Publishers, New York, 1940.



as its molecular weight, it is obvious that the molecular weights of colloids must be enormous. Colloid particles range in diameter from 10 to 10,000 Å.; the diameter of atoms is of the order of 1 Å. In a colloid system all the particles are not uniform in size, and any measurement of their weight must be considered as an average weight. It is better to speak of particle weight rather than molecular weight.

The ordinary methods for determining molecular weights in solution are beset with difficulties when applied to colloid systems because it is almost impossible to wash out all the ions, and each ion is just as effective as a colloid particle in lowering the vapor pressure or the freezing point, or creating an osmotic pressure. Furthermore, the effect to be measured is very small. It will be remembered that  $6 \times 10^{23}$  molecules dissolved in 1000 g. of water will lower the freezing point  $1.86^\circ$ , and if ten thousand of these units are combined into one colloid particle the freezing-point lowering will be only  $0.000186^\circ$ . Accordingly, a mere trace of electrolyte left behind will produce an effect greater than this.

A few satisfactory measurements have been made using collodion membranes and measuring the apparent osmotic pressure of concentrated solutions under conditions where ions do not affect the pressure. The holes in the collodion membrane are large enough to let the ions pass but they block the passage of the large colloid particles. An excess of electrolyte is added to the colloid solution and to the solvent on the two sides of the membrane. The ions diffuse through and reach equilibrium, so that the measured osmotic pressure is due only to the colloids. By rigorous control of the amount of electrolyte present, Sorensen found a molecular weight of 34,000 for egg albumin and Adair\* obtained 67,000 for hemoglobin.

*Example 2.* A solution of 1 g. of a nitrocellulose in a liter of acetone has an osmotic pressure of  $0.56 \times 10^{-3}$  atm. at  $27^\circ$ . Assuming that the solution is ideal, calculate the molecular weight of the nitrocellulose.

$$P_v = \frac{gRT}{M}$$

$$M = \frac{gRT}{P_v} = \frac{1 \times 0.08205 \times 300.1}{0.56 \times 10^{-3} \times 1} = 44,000$$

**Sedimentation Equilibrium.** The distribution of colloid particles under a given force such as gravity is related in a rather simple way to diffusion and osmotic pressure. When a solution is allowed to stand, a state of equilibrium is finally reached when sedimentation and diffu-

\* Adair, *Proc. Roy. Soc. (London)*, [A] 109, 292 (1925).

sion balance each other, that is, when in a given interval of time the amount of material which falls in the downward direction through a unit area is the same as that which diffuses upward on account of the difference in the concentration. The most familiar example of a sedimentation equilibrium is the atmosphere of the earth.

The quantitative formula for the concentration as a function of height makes possible the determination of the molecular weight of a solute, provided the solution is dilute enough for the ordinary laws of dilute solutions to hold. It should be noted particularly that the equation contains only well-defined and measurable quantities and its validity is independent of the shape of the particles. The formula for sedimentation equilibrium can be derived by thermodynamics for a colloidal solution containing particles of uniform size, using the following symbols:

- $n$  = number of particles per milliliter, i.e., the concentration;
- $x$  = the distance of the particle from the bottom of the vessel;
- $g$  = acceleration of gravity;
- $S$  = density of the particle;
- $S_0$  = density of the liquid;
- $v$  = volume of the particle.

Two forces are acting: the force of gravity (or other force) tends to pull the particles to the bottom of the vessel, thus increasing the concentration; and the kinetic force causes the particles to diffuse away from the region of higher concentration at the bottom.

The force of gravity pulling one particle downward is  $v(S - S_0)g$ , where  $S - S_0$  is the effective density of the particle, allowing for the buoyancy of the liquid.

The change in free energy  $\Delta F$  for the transfer of a mole of particles from one concentration to another is given on page 220 by the equation

$$\ln \frac{n_2}{n_1} = \frac{\Delta F}{RT} \quad [7]$$

At equilibrium the decrease in free energy must be equal to the work done  $w$  by a mole of the particles ( $N$  particles) against the force of gravity acting through the distance  $x_1 - x_2$ . Then

$$\ln \frac{n_2}{n_1} = \frac{w}{RT} = \frac{Nv(S - S_0)g(x_1 - x_2)}{RT} \quad [8]$$

The same equation can be derived from considerations of diffusion rates. The values of  $n_2$  and  $n_1$  may be obtained by counting the number of particles in a given field with a traveling microscope.

*Example 3.* The number of particles in a given volume of a solution of colloidal gold which had come to equilibrium in the earth's gravitational field was found to be 392 at one level and 196 at a level 0.10 mm. higher. The temperature was 20°, and the diameter of the particles was 0.066 $\mu$ . The specific gravity of gold is 19.3, and that of the colloidal solution may be assumed to be 1. What is the value of Avogadro's number as calculated from these data?

$$2.303 \log \frac{392}{196} = \frac{N \times \frac{4\pi}{3} (3.3 \times 10^{-6})^3 (19.3 - 1.0) (981) (0.01)}{8.31 \times 10^7 \times 293}$$

$$N = 6.2 \times 10^{23}$$

**The Ultracentrifuge.** The sedimentation due to the force of gravity is so small that it can be used only for the largest particles. The sedimentation force may be increased enormously, however, by using centrifugal force, and it is thus possible to determine particle size or molecular weights of the smallest particles — even down to ordinary molecules in true solution. Svedberg has contributed greatly to this field.

In the centrifuge the acceleration of gravity is replaced by centrifugal force,  $\omega^2 x$ , where  $\omega$  is the angular rotational velocity,  $2\pi \times$  the number of revolutions per second, and  $x$  is the distance from the center of rotation. Then integrating  $\omega^2 x dx$  and substituting for  $g(x_1 - x_2)$  in equation (8),

$$\ln \frac{n_2}{n_1} = \frac{\frac{1}{2} \omega^2 (x_1^2 - x_2^2) N v (S - S_0)}{RT} \quad [9]$$

An additional advantage of the ultracentrifuge is that the sedimentation force may be controlled.

Sedimentation equilibrium measurements using equation (9) require much time and effort, and a different technique is often used in which the velocity of sedimentation rather than the concentration of particles at equilibrium is measured.

In operating the velocity ultracentrifuge the solution is placed in a small cell inserted in the rotor. The cell has transparent windows, and in the chamber which encloses the rotor there are corresponding windows with electromagnetic shutters. By directing a beam of light through the windows one can note the effects of the centrifugal force. A diagram showing the principle of the Svedberg ultracentrifuge is given in **Fig. 73**. Photographic methods are used to record the position of the boundary between solvent and solution at suitable intervals. Exact measurements on the photographic plate are then used for calculating the rate at which the colloid particles move. If all the particles

are not of the same size, a sharp boundary cannot be obtained even if diffusion is minimized. It is of great importance to eliminate vibrations and the convection currents which arise normally from thermal gradients within the cell. These and other difficulties have been overcome by Svedberg.\*

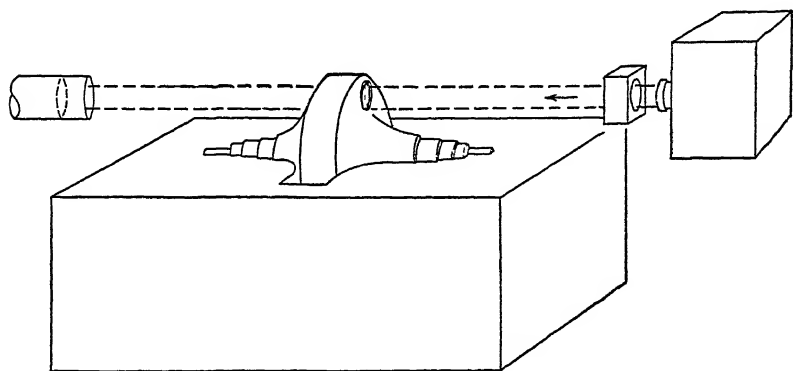


FIG. 73

The specific sedimentation velocity in centimeters per second per unit centrifugal field is a characteristic of the dissolved particle.

The specific sedimentation velocity of thyroglobulin may be calculated from the measurements of Lundgren and Williams shown in Fig. 74. This biological material was purified and mixed with a clear solution of the same acidity. The beam of light passed directly through the cell as it was rotated in the centrifuge but as the colloid moved outward it left a line of demarkation where the refractive index was different so that the light was refracted out of the optical line leaving a dark ridge. As the centrifuging progressed this heavier material gradually moved toward the outer edge of the cell, shown by a sharp vertical shadow at the right. Pictures were taken

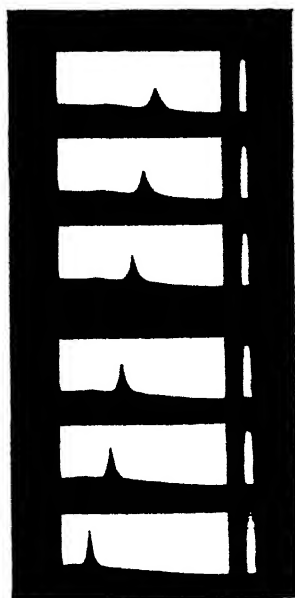


FIG. 74

\* Svedberg and Pedersen, "The Ultracentrifuge," *Chem. Rev.*, 20, 81 (1937).

every ten minutes starting at the bottom of Fig. 74 and measurements on the position of the peak showed that the boundary moved 7.2 mm. in 50 minutes. There was a temperature correction  $\eta_t$  for viscosity amounting to 0.90. The speed of the centrifuge was 40,000 r.p.m. and the distance from the center of rotation was 6.4 cm. The sedimentation constant  $s$  is calculated as follows:

$$s = \frac{\frac{dx}{dt}}{\omega^2 x} \times \eta_t = \frac{\frac{0.72}{50 \times 60}}{\left(2\pi \times \frac{40,000}{60}\right)^2 \times 6.4} \times 0.90$$

$$= 18.9 \times 10^{-13} \text{ cm. per sec. per unit field} = 18.9 \text{ Svedbergs}$$

The particle size cannot be calculated and used without further information, because two molecules of like weight but different shape will have different sedimentation constants. Particle sizes may be obtained, however, from observations of sedimentation velocity and diffusion constant made independently of one another. In dilute solutions the frictional resistance to sedimentation and diffusion is the same, so that if a diffusion measurement is used to evaluate this resistance it is not necessary to make any assumption regarding the shape of the particle. Sometimes the centrifugal force may be increased to such an extent that the effect of the back diffusion becomes small and the velocity of sedimentation of the solute particles can be used directly without serious corrections. With the new high-speed instruments, centrifugal forces as high as 400,000 times gravity are available, and observations of the sedimentation velocity may be made in a few hours.

Some of the results obtained with Svedberg's methods are given in Table I.

Simple motor-driven or air-driven centrifuges find important uses in separating colloids from solution and from mixtures of other colloids. The measurements of particle size in the more elaborate centrifuges have given us valuable information concerning the proteins in normal and pathological sera, toxins and anti-toxins, viruses, hormones, enzymes and their action on proteins, polysaccharides, starches, and natural and synthetic high polymers.

**Electrical Behavior.** Colloid particles with their large surfaces are likely to have ions attached to them. An ion induces a charge of opposite sign in an adjacent molecule and will thus be held to the surface by the ion-induced dipole attraction. The ions thus *adsorbed*

TABLE I  
WEIGHTS OF COLLOID PARTICLES

Protein	Particle Weight	Protein	Particle Weight
Egg albumin	40,500	Phycocyan	279,000
Hemoglobin	68,100	Phycoerythrin	292,000
Serum albumin	66,900	Amandin	329,000
Lactoglobulin	37,800	Thyroglobulin	675,000
Pepsin	39,200	Hemocyanin	
Insulin	35,100	( <i>Octopus</i> )	2,785,000
Serum globulin	150,000	Hemocyanin	
		( <i>Helix</i> )	6,630,000

exert a profound influence on the stability of the colloids, particularly the lyophobic colloids. According to the simplest view all the particles in a given colloidal solution tend to adsorb an excess of either positive or negative ions and thus acquire a charge. The particles thus repel each other and tend to prevent combination and precipitation of the colloidal material.

The situation is more complicated, however, because the charged surface of the colloid particle tends to attract ions of opposite sign to it, forming two layers of oppositely charged electricity as in a condenser. These electrical fields due to ions constitute what is known as a double layer.

Helmholtz believed this double layer to form the equivalent of a parallel-plate condenser with an equal and opposite layer of fixed charges residing at a molecular distance 1 or 2 Å. from the surface of the particle. It was soon discovered, however, that the value of the potential difference is a function of the method used to measure it. This fact suggested that the potential does not change abruptly as Helmholtz believed; rather, it is built up over an appreciable distance. A portion of the difference in potential exists between the movable and stationary liquid layers at the interface. The forces, which are sufficient in ordinary experiments to move the two sides of the ionic layer relatively to one another, are much too small to remove the liquid and its charges from the actual surface of the solid. The layer of charges adhering to the solid surface moves with reference to the main body of liquid. Thus the double layer stretches much farther out than a molecular distance from the solid surface into the liquid; and it is diffuse rather than compact. The total potential drop is between the surface of the solid and the movable liquid, but the *electrokinetic* or *zeta potential* is that portion of the potential drop

between the liquid adhering to the wall of the particle and the movable liquid. It is described diagrammatically in Fig. 75 where *A* represents the surface of the particle and *B* represents a point in the solution far removed from it. Freundlich and von Smoluchowski introduced this concept of the electrokinetic or zeta potential into colloid chemistry. It has been pointed out, particularly by Kruyt, that the stability of hydrophobic colloids runs parallel with the zeta potential.

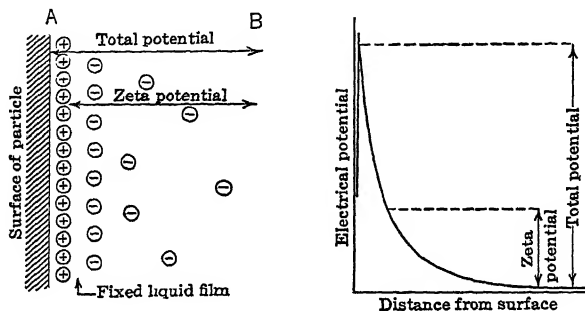


FIG. 75

The dependence of the electrokinetic phenomena\* and therefore of the zeta potential on the concentration and nature of the electrolyte present is not understood with exactness, yet certain general statements may be made. At high concentrations of electrolyte the electrokinetic phenomena disappear because the double layer is compressed about the particle, and the increase in electrical conductivity also causes a diminution in electrokinetic action. The zeta potential is determined by all the ions which happen to be present in the boundary layer, and their charge and adsorbability determine the effect produced.

**Electrophoresis.** There are several important consequences of the existence of the potential difference in the diffuse double layer. The application of an external voltage causes the charged colloid particles to move toward one of the electrodes. The motion is one of a fixed layer of liquid relative to a mobile layer. A negative colloid moves to the positive electrode, and a positive colloid to the negative. This phenomenon is known as *electrophoresis*.

Electrophoresis was first observed by Reuss in 1807. When the terminals of an electric battery are connected to two platinum electrodes dipping into a colloidal solution of arsenious sulfide, there is a

\* Abramson, "Electrokinetic Phenomena," Reinhold Publishing Corp., New York, 1934.

gradual migration of the colloid to the positive pole. A similar experiment with a solution of ferric hydroxide shows that this colloid moves toward the negative pole. It follows, therefore, that the particles of colloidal arsenious sulfide are negatively charged, whereas those of colloidal ferric hydroxide carry a positive charge. Most of the lyophobic colloids possess an electrical charge. In water, the colloids of metals and many organic colloids acquire a negative charge, but many positive colloids are known also.

The velocity of electrophoresis can be determined by measuring the rate of movement of the boundary which separates the colloid solution from a clear solution which has been carefully run in above it. In a more accurate method a microscope is used to measure the distance traveled toward the electrode by a single colloid particle under a definite potential gradient. In measurements of electrophoresis the electrodes are usually arranged so that there is no evolution of gas which might cause mechanical stirring of the solution. For example, a cadmium electrode surrounded by cadmium ions may be used. The velocities of electrophoresis vary considerably with the conditions of the experiment, but they are of the order of  $2$  to  $5 \times 10^{-4}$  cm. per second when the potential gradient is 1 volt per centimeter. Although the colloid particles are much larger than individual ions the rate of movement toward an electrode is of the same order of magnitude.

There are many practical applications of electrophoresis. The sign of the charge on colloids and bacteria is easily found. Certain colloids may be plated out electrically similar to the electroplating of metals and in fact many rubber articles such as rubber gloves are manufactured in this manner.

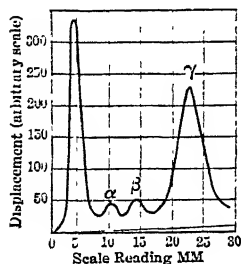
Among the important developments in electrophoresis are the examination and separation of proteins, including normal, pathological, and immune sera, the preparation of pure biological materials, and the control of industrial processes involving polymerization. Apparatus for following the migration of these materials in an electrical field has been perfected by Tiselius.\* A cell is provided with flat transparent sides and a beam of light specially focused is recorded on a photographic plate. The material frequently contains two or more materials which are so nearly alike that they cannot be separated by chemical means; yet when placed between two electrodes they move at slightly different rates. The light passes through the colloid solution and the clear solution adjoining it without deflection, but at the line of demarcation between two solutions the light is refracted to one side leaving a dark region. After a time the different colloid materials

\* Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937); *Biochem. J.*, **31**, 1464 (1937).



move along to different distances and give optical patterns similar to that shown in **Fig. 76** for the electrophoresis of anti-egg albumin in rabbit serum.\*

The concentrations of the different protein fractions are shown as peaks plotted along the scale which gives the distance between the electrodes. The highest peak is due to albumin, and the other peaks  $\alpha$ ,  $\beta$ , and  $\gamma$  are due to different fractions of globulin.



**Fig. 76**

The characteristic pattern may be used for identification of a mixture and for determination of purity. A uniform material having colloids of only one size and charge gives a single dark band. A colloidal protein or other material may be not only identified, but it may also be purified by electrophoresis. For example, it may be found that only one of the substances gives the desired biological effect, and this material can then be withdrawn from the remaining solution when the shadow of its boundary passes the exit tube at a specified level.

**Electroosmosis.** The phenomenon of electroosmosis is related to electrophoresis. If a potential difference is applied to a colloid solution when the colloids are not free to move as they are in electrophoresis, the mobile liquid will move. This is the cause of *electroosmosis*. In electrophoresis the particles move under a potential gradient, whereas in electroosmosis the liquid moves. Finally, if the colloid surfaces are held mechanically stationary and the liquid is forced through a colloid membrane or porous plate a potential difference will be produced at the two sides of the membrane. This potential difference may be measured and is known as the *streaming potential*. All three properties are connected, at least in a qualitative way, with the zeta potential.

If a porous partition is placed in the bottom portion of a U tube, and an electrode is inserted in each arm of the tube, it will be found, on filling the tube with a feebly conducting liquid and passing a current, that the liquid will commence to rise in one arm of the tube, and will continue to rise until a definite equilibrium is established. For a given difference of potential between the two electrodes, there will be a definite difference in the level of the liquid in the two arms of the tube. Usually, but not always, substances acquire a negative electric charge when immersed in water. The water, then, becomes positively charged and will, in consequence, migrate toward the cathode.

\* Tiselius, "Electrophoretic Analysis and the Constitution of Native Fluids," Harvey Lecture Series, **35**, 52 (1939).

The direction of electroosmosis indicates the sign of the charge on the liquid. The experiments have been extended to organic liquids as well as to aqueous systems. The drying of peat and other material' by the application of an electrical field has been suggested; but there is a large loss of electrical energy if electrolytes are present to conduct the current.

**Stability of Colloids.** The most important factors in stabilizing colloids are electrical charge (zeta potential) and hydration (or solvation). Either the existence of a zeta potential which causes the particles to repel each other, or a film of adsorbed solvent which prevents the enclosed particles from touching each other, is sufficient to keep the dispersed particles in the colloidal state. In the lyophobic

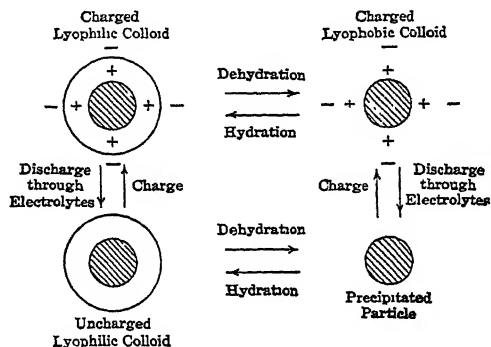


FIG. 77

colloids, where there is little attraction between the dispersed particles and the dispersion medium, the film is not a factor and the stability or instability of the colloid depends only on the presence or absence of a diffuse layer of ions about the particle. The relation between the lyophilic colloids and the lyophobic colloids is well illustrated in **Fig. 77**. The lyophilic colloid particles are solvated, i.e., they attract around themselves an atmosphere of the dispersion medium whereas the lyophobic colloids do not. Either the electrical double layer, or the hydrating atmosphere, or both together, keep the system in the colloidal state. The particles become coagulated and the system loses its colloidal properties only when both the electrical double layer and the hydrating atmosphere are removed. Egg albumin may be taken as an example. Its particles can be dehydrated with alcohol and the electrical charge can be neutralized by the addition of ions, but only when *both* changes are effected does coagulation occur.

The ability of dispersed particles to remain in the colloidal state

is greatly affected by the concentration of ions. In the absence of ions a lyophobic colloid is not stable and the material will settle out. The presence of a few ions stabilizes the colloid but if there is a large excess of electrolyte the colloid particles will be coagulated by the ions of opposite charge.

When the colloid has its minimum stability because of the absence of ions it is said to be at the isoelectric point. Under these conditions the zeta potential is practically zero and there is little or no tendency for the particles to migrate in an electrical field. Viscosity and other properties show a minimum. The isoelectric point is important in both lyophilic and lyophobic colloids. Lyophilic colloids such as albumin and gelatin are particularly responsive to a change in hydrogen-ion concentration, and in an acid solution they are charged positively on account of a chemical reaction and subsequent dissociation. In an alkaline solution they acquire a negative charge in the same way. The behavior is like that of amphoteric electrolytes which can dissociate to give either  $H^+$  ions or  $OH^-$  ions.

**Precipitation of Colloids by Electrolytes.** Electrolytes, even in low concentrations, are effective in precipitating colloids from solution. The concentrations in milliequivalents per liter required to cause precipitation in two hours, as found by Freundlich, are recorded in Table II for a positive ferric hydroxide colloid (16 millimoles per liter) and for a negative arsenious sulfide colloid (8 millimoles per liter). In each case, 2 ml. of the electrolyte was added to 20 ml. of the colloid solution.

TABLE II  
PRECIPITATION OF COLLOIDS BY ELECTROLYTES

Electrolyte	(+) Ferric Hydroxide	(-) Arsenious Sulfide	Electrolyte	(+) Ferric Hydroxide	(-) Arsenious Sulfide
	Conc. Electrolyte	Conc. Electrolyte		Conc. Electrolyte	Conc. Electrolyte
NaCl	9	51	MgSO <sub>4</sub>	0.2	0.8
KCl	9	50	AlCl <sub>3</sub>	...	0.1
KNO <sub>3</sub>	12	50	Al(NO <sub>3</sub> ) <sub>3</sub>	...	0.1
Ba(NO <sub>3</sub> ) <sub>2</sub>	14	0.7	K <sub>2</sub> SO <sub>4</sub>	0.2	...
BaCl <sub>2</sub>	10	0.7	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.2	...

It is evident that the trivalent ions are much more effective in precipitating colloids of opposite sign than are divalent ions and that the divalent ions are more effective than the univalent ions. There is no simple quantitative relation between the valence of the ion and the

precipitating concentration because several other factors are involved also, such as the protective action of ions having the same sign as the colloid particles.

These observations support the general rule that the precipitation of a colloid is effected by that ion of an added electrolyte which has an electric charge opposite in sign to that of the colloid particle. The higher the valence the more effective is the precipitating ion.

The action of electrolytes on lyophilic colloids is less sharply defined than their action on lyophobic colloids. Large concentrations of alkali salts are necessary to precipitate albumins; but small amounts of the heavy metals give precipitation on account of chemical reactions.

Charged colloids as well as ions are effective in precipitating colloids of opposite charge. For example, when solutions of positive ferric oxide colloids and negative arsenious sulfide colloids are mixed a mutual precipitation of the two colloids is produced.

Sometimes the mixture of two different kinds of ink will cause a precipitation for the same reason.

**Protective Colloids.** The precipitating action of electrolytes on lyophobic colloids may be inhibited by adding a lyophilic colloid to the solution of a lyophobic colloid.

Zsigmondy has made the protective power of lyophilic colloids the basis of a method of classification of colloidal substances. A red colloidal gold sol becomes blue on the addition of a small amount of sodium chloride, owing to the increase in the size of the colloidal particles. Various colloidal substances when added to a red-colored gold sol protect the colloidal particles from precipitation by a solution of sodium chloride and prevent the change in color. A definite amount of each colloidal substance is required to prevent the change from red to blue. Zsigmondy introduced the term "gold number," defined as the weight in milligrams of a colloidal substance which is just insufficient to prevent the change from red to blue in 10 ml. of a gold sol, after the addition of 1 ml. of a 10 per cent solution of sodium chloride. Table III gives the gold numbers of a few colloids.

The gold number is used in diagnosing certain diseases, the spinal fluid from an afflicted person giving a gold number markedly different from that given by the spinal fluid from a healthy person.

The ability to exert protective action is not confined to organic colloids alone. It is in fact very important in preserving the character of cements and sedimentary rocks.

In general, it may be said that, when a lyophobic colloid is mixed with a lyophilic colloid in the proper proportions, the lyophobic colloid

TABLE III  
GOLD NUMBERS OF COLLOIDS

Colloid	Gold Number	Colloid	Gold Number
Gelatin	0.005-0 01	Starch, wheat	4-6
Casein	0 01	Starch, potato	25
Egg albumin	0 15-0 25	Sodium oleate	0.4-1
Gum arabic	0 15-0 25	Cane sugar	8
Dextrin	6-12	Urea	8

acquires most of the characteristic properties of the protecting colloid. The masking of the properties of a lyophobic colloid by a protecting colloid is probably to be ascribed to the formation of a thin film of adsorbed lyophilic colloid over the lyophobic colloid.

**Surface and Interfacial Tension.** When two partially miscible liquids are placed in contact, each dissolves to a certain extent in the other and may cause marked changes in the surface tensions. The interfacial tension may be defined as the work required to increase the area of the interface by 1 cm.<sup>2</sup> It is equal to the difference in surface tensions of the two saturated liquids in contact with the saturated vapors. It can be measured by most of the methods already described for measuring the surface tension of pure liquids against air at atmospheric pressure saturated with the vapor. The drop-weight method is perhaps the simplest for measuring interfacial tensions, the number of drops of one liquid being counted as they fall (or rise) from a standard capillary tip which is immersed in a second liquid. The addition of a third substance which concentrates in one or both liquids at the interface may exert a profound influence on the interface and on the colloidal behavior as shown in the following sections.

**Gibbs' Equation.** The mathematical relation given by equation (10) between concentration of a solute and the surface tension of the solution was developed by J. Willard Gibbs\* in 1876. This relation can be developed with the help of free energy considerations but an exact derivation is beyond the scope of the present considerations.

$$u = - \frac{c}{RT} \frac{d\gamma}{dc} \quad [10]$$

where  $u$  is the excess of solute in the surface layer per square centimeter of surface, and  $d\gamma/dc$  expresses the rate of change of surface tension with concentration.

\* Gibbs, *Trans. Conn. Acad.*, 3, 439 (1876).

From this equation it is evident that, if the surface tension,  $\gamma$ , increases with the concentration, then  $u$  is negative, and the surface concentration is less than the concentration of the bulk of the solution. On the other hand, if  $\gamma$  decreases as the concentration increases,  $u$  is positive, and the surface concentration is greater than the concentration of the bulk of the solution. Finally, if the surface tension is independent of the concentration, then the concentration of the solute in both the surface layer and the bulk of the solution will be the same.

It may be concluded further that the surface tension of a liquid can be lowered to a considerable extent by the addition of a solute because the solute will then concentrate in the surface and register a large effect, but the surface tension can never be increased very much by the addition of a solute because, in this case, it is held chiefly by the bulk of the solution where it can exert no influence on surface phenomena. This deduction is well confirmed by experiment. Soaps and other material are known to reduce the surface tension of water by more than half, but no substance has yet been discovered which will raise the surface tension more than a few per cent.

Experimental tests of this equation are difficult because the real surface layer contains such a small amount of dissolved material, but they indicate that the equation is essentially correct. In one of the tests, froth and foam were swept out from a soap solution and the concentration in this froth was found to be greater than that in the bulk of the solution left behind; in another, a scoop traveling along an accurately machined track skimmed off the surface of the solution.\*

**Adsorption.** The tendency exhibited by all solids to condense upon their surfaces a layer of any gas or solute with which they are in contact is termed *adsorption*. The amount of adsorption is conditioned by the extent of the surface exposed, by the pressure or concentration, by the temperature, and also by the specific nature of the adsorbent and that of the adsorbed substance.

The retention of gases by charcoal and the removal of dyes, such as methylene blue with charcoal, are examples of adsorption. The clarification of solutions through the adsorption of undesirable colored impurities is a common operation in many industrial processes.

At a given temperature and concentration, a given sample of charcoal is found to adsorb a definite quantity of material. If the concentration is increased, it will adsorb more; if it is decreased, it will adsorb less; but on restoring the concentration to its initial value the amount of adsorbed material is found to be the same as that originally

\* Nutting, Long, and Harkins, *J. Am. Chem. Soc.*, **62**, 1496 (1940).

McBain and Wood, *Proc. Roy. Soc. (London)*, [A] **174**, 286 (1940).

taken up. In other words, an adsorption equilibrium is reached. If the concentrations are plotted against the quantities of material adsorbed, curves of the character of those shown in Fig. 78 are obtained.

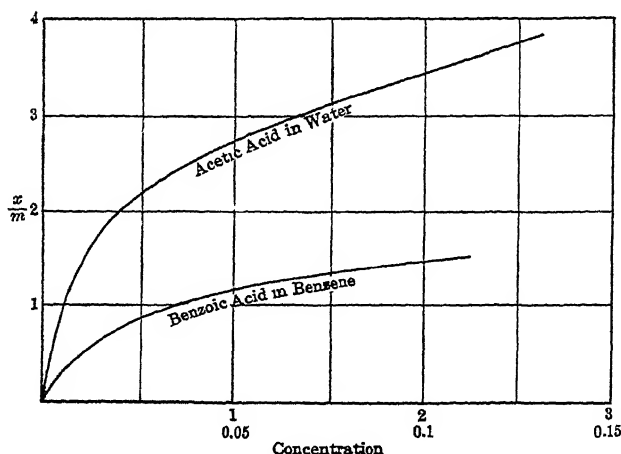


FIG. 78

Adsorption of this type may often be represented by the empirical equation of Freundlich, which applies either to gases or to solutes in solution,

$$\frac{x}{m} = kc^n \quad [11]$$

or

$$\log \frac{x}{m} = n \log c + \log k \quad [12]$$

where  $k$  and  $n$  are constants to be determined by experiment for each temperature, solute, and adsorbent. They should, however, be independent of the concentration. Graphs for this equation are shown in Fig. 79.

*Example 4.* When  $m$  grams of a certain charcoal was allowed to stand in an aqueous solution of acetic acid of various concentrations  $c$ ,  $x$  grams of acetic acid was adsorbed by the  $m$  grams of charcoal. The experimental values of  $c$  and  $x/m$  at  $25^\circ$  are as follows:

$c$	0.018	0.031	0.062	0.126	0.268	0.471	0.882	2.79
$x/m$	0.467	0.624	0.801	1.11	1.55	2.04	2.48	3.76

These data are graphed in Figs. 78 and 79.

What are the constants  $k$  and  $n$  in equation (11)?

The straight line in Fig. 79 shows that the empirical equation (11) of Freundlich describes the data very well. For acetic acid the constant  $n$  is the slope of the line 0.42 and the constant  $k$  is the antilogarithm 2.6 of the intercept, where  $\log c = 0$ .

Then

$$\frac{x}{m} = k c^n = 2.6c^{0.42}$$

No very definite generalization concerning the behavior of adsorbents can be formulated. Charcoal, whether of vegetable or animal origin, is probably the most powerful adsorbent known. The

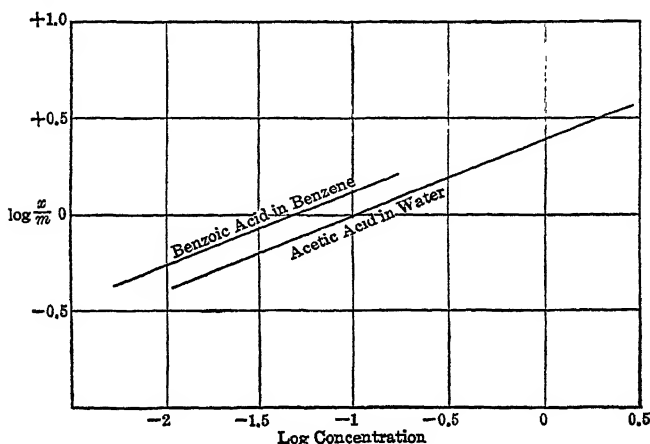


FIG. 79

large surface is due to the original structure with the many small cells. Silica gel, the dehydrated gel of silicic acid, is another effective adsorbent which finds extensive scientific and industrial applications.

The phenomena attending the absorption of suitable electrolytes by difficultly soluble salts, such as kaolin, are of special interest. If, for example, a solution of methylene blue chloride, which is strongly ionized in aqueous solution, is shaken up with kaolin, the adsorption will be found to differ in several respects from the adsorption of a non-ionized solute by an insoluble adsorbent, such as charcoal. Thus, only the cation of the dye is adsorbed, while the chloride ion remains behind in the solution with its concentration practically unaltered. Since the electrical neutrality of the solution must be preserved through the presence of an equivalent number of cations and anions, the adsorption of the cations of methylene blue must be



offset by the removal from the adsorbent of an equivalent number of positively charged ions. In the example under consideration, electrical neutrality is found to be preserved by the removal of positively charged ions from the kaolin surface. This type of adsorption is known as *exchange adsorption*. The behavior of artificial zeolite affords an interesting example of exchange adsorption. This substance takes up calcium ions from solution and gives up an equivalent number of sodium ions.

**Theory of Adsorption.** The Freundlich equation is useful as an empirical formula, but a better equation has been developed by Langmuir.\* Its derivation is based on the well-established view that a solid has a crystal lattice and that its surface is like a checkerboard with atoms arranged in orderly fashion. Each atom at the surface has free valences or unattached forces which are available for attaching one, and only one, molecule from the gas phase or from solution. There is a continuous flight of molecules from the external phase to the surface and in the opposite direction. The rate at which molecules are adsorbed depends on three factors: (1) the number  $s$  striking the surface per second (calculated from the kinetic theory of gases); (2) the fraction  $m$  of incident molecules which adhere; and (3) the area  $(1 - g)$  which is not covered by adsorbed molecules,  $g$  being the fraction covered. The rate of desorption is  $gr$ , where  $r$  is the rate of evaporation from a completely covered surface.

At equilibrium

$$gr = ms(1 - g) = ms - gms$$

$$g = \frac{ms}{r + ms}$$

Substituting  $l$  for the constant,  $m/r$ ,

$$g = \frac{ls}{1 + ls} \quad [13]$$

Using different constants,  $a$  and  $b$ , the weight of adsorbed material,  $y$ , per unit surface of adsorbing material is given by the formula

$$y = \frac{abp}{1 + ap} \quad [14]$$

where  $p$  is the pressure of the gas. Concentrations  $c$  may be used instead of pressures and  $y$  may be considered proportional to the weight of adsorbed material per weight of adsorbing material.

\* Langmuir, *J. Am. Chem. Soc.*, **38**, 2267 (1916); **40**, 1361 (1918).

This formula fits many experimental data very well. In fact, the agreement constitutes an argument in favor of the underlying assumption of an adsorbed layer one molecule deep. At very high pressures it does not always apply so well, probably because under these conditions a new type of adsorption is occurring, namely, the liquefaction of the gas in capillary pores. Under these conditions the layer is of course many molecules deep and there is other evidence of condensation. Patrick found that, on silica gel, where the capillary type of adsorption prevails, the quantity of different gases adsorbed under similar conditions depends chiefly on the boiling point. Taylor has been able from thermal measurements to distinguish between (1) chemical adsorption by attachment to an atom at a surface, and (2) physical adsorption. The evolution of heat in (1) may be several times that in (2).

It is significant that improved experiments tend more and more to support the Langmuir formula and its underlying hypotheses, when the adsorption is not too great. Measurements of the quantity of water adsorbed on glass surfaces seemed to indicate that the layer must be several molecules deep, but repetition of the work with fresh glass surfaces that had never been etched by contact with liquids showed that the adsorbed layer is probably one molecule thick.\* In an important series of investigations in which adsorbed material was weighed with a small spiral spring of quartz, McBain† has shown that if the adsorbing surface is absolutely clean the Langmuir formula applies satisfactorily, whereas the Freundlich formula can be applied if the adsorbing surface contains impurities. Additional proof of the correctness of Langmuir's formula is due to Tiselius.‡

**Chromatic Adsorption.**§ The rate of adsorption on a given adsorbent varies for different materials. Accordingly, when a solution containing several different substances is poured through a column of the adsorbent, each substance comes out at a different level. For example, if a green leaf is extracted with acetone or petroleum ether and the solution is poured through a tube containing powdered sugar, followed by a little pure acetone or petroleum ether, the tube will show different bands of color corresponding to the carotenes, chloro-

\* Frazer, Patrick, and Smith, *J. Phys. Chem.*, **31**, 897 (1927).

† McBain and Britton, *J. Am. Chem. Soc.*, **52**, 2198 (1930).

‡ Tiselius, *J. Phys. Chem.*, **40**, 223 (1936).

§ Cassidy, *J. Chem. Educ.*, **16**, 88 (1939).

Strane, "Chromatographic Adsorption Analysis," Interscience Publishers, New York, 1941.

Zechmeister and Chohnoky, "Principles and Practice of Chromatography," John Wiley & Sons, 1941.

phyll A, chlorophyll B, and other colored compounds. The column may then be cut apart in sections to separate the different materials adsorbed from the solution. Since most of the work to date has been done with colored substances which can be seen, the process is called chromatic adsorption. It provides a simple, effective method for the separation of biological materials which are otherwise difficult to separate.

Alumina, magnesia, powdered glass, charcoal and other adsorbents may be used. Colorless materials could be separated also, if the lines separating the different material can be brought out by fluorescence or ultraviolet photography. Tiselius has described a modification of this method in which the solution is forced through an adsorbing column under conditions such that the materials are slowed down but not entirely adsorbed. The moving column of filtrate is then examined with a beam of light, as in the measurements of electrophoresis described on page 249. Dark lines separate the solutions of the different dissolved materials, and, as they move along the tube the solution between two of these dark lines is drawn out through a side arm. In this way one dissolved material may be separated from the others. Tiselius,\* using charcoal, has separated glucose from a mixture of glucose and lactose by this method.

**Molecular Orientation at the Interface.** When one drop of stearic acid or a similar oil is placed on a trough of absolutely clean, grease-free water the oil spreads out quickly to give an extremely thin layer. The edges of the oil film are made visible by dusting talc or a similar powder over the surface and the area then can be readily measured. The weight and density of the oil and the area of the film being known, the thickness may be calculated easily. Moreover, the number of molecules can be calculated from the weight of the oil and Avogadro's number. When the film has spread so far that it does not spread any further, it may be assumed that the layer is only one molecule thick. Then the average cross section of a molecule can be calculated from the area, and the average length of the molecule can be calculated from the thickness of the film. A few values obtained in this way are summarized in Table IV

It is seen that the cross-sectional area of an aliphatic chain is about 22 sq. Å. and that the compounds with three chains in the molecule have areas of 66 sq. Å. Increasing the length of a chain with more carbon atoms causes a corresponding increase in the film thickness. Moreover, the length and cross section of the molecules calculated in this way are in excellent agreement with the values obtained inde-

\* Tiselius, *Arkiv. for kemi, mineralogi o geologi* [15B], 6, 1-8 (1941).

pendently by x-ray analysis of crystals and in other ways. These facts support the hypothesis that the film is exactly one molecule thick, and closely packed, the longer axis of the molecules being nearly at right angles to the surface of the water film. These measurements were among the first to provide direct physical evidence that the organic molecules are of the shape and size expected from theoretical organic chemistry.

TABLE IV  
DIMENSIONS OF MOLECULES IN UNIMOLECULAR FILMS

Film	Formula	Film Thickness (Length of Molecule)	Area
Palmitic acid	$C_{15}H_{31}COOH$	24 Å.	21 sq. Å.
Stearic acid	$C_{17}H_{33}COOH$	25	22
Cerotic acid	$C_{25}H_{51}COOH$	31	25
Tristearin	$(C_{15}H_{35}O_2)_3C_3H_5$	25	66
Cetyl alcohol	$C_{16}H_{33}OH$	22	21
Myricyl alcohol	$C_{30}H_{61}OH$	41	27

The explanation of this vertical alignment of molecules at the interface was offered by Harkins and by Langmuir. A molecule such as stearic acid has a polar carboxyl group at one end of a hydrocarbon residue. There is a strong dipole attraction between the carboxyl group and the water molecules but little attraction between the hydrocarbon part of the molecule and water. In simpler language, the carboxyl end of the molecule tends to dissolve in the water and the hydrocarbon portion does not. The result is that the molecules become orientated with their "heads" attached to the water and their "tails" aligned vertically. This hypothesis of vertical alignment and close packing has been checked by direct measurements with reflected x rays. This orientation at an interface is exhibited not only by the organic acids but also by the higher alcohols and any insoluble material which has a polar group on one part of the molecule. It is responsible for a variety of phenomena in colloid chemistry and biology.

The force exerted by these unimolecular films has been measured accurately with simple apparatus.\* A barrier is forced against

\* Langmuir, *J. Am. Chem. Soc.*, **39**, 1869 (1917).

Harkins, "Recent Advances in Surface Chemistry and Chemical Physics," page 29, Am. Assoc. Adv. Sci., The Science Press, New York, 1939.

the film in a special trough, and the force required to compress the film by definite area increments has been measured with a special balance. On plotting the force in dynes against the areas per molecule, expressed in square Ångströms, curves are obtained for these two-dimensional films which exhibit breaks at definite pressures.

Langmuir\* has carried out interesting experiments with these uni-molecular films. By dipping a clean plate of glass up and down through the surface film it is possible to build up multiple layers which finally become thick enough to show interference patterns with light. From the number of films deposited and the wavelength of light, it is possible to calculate the length of the molecule in the film. This value agrees with the length calculated in other ways.

**The Donnan Membrane Equilibrium.**† Certain colloidal substances, such as congo red, are alkali salts of complex organic acids and they dissociate, for example, into  $\text{Na}^+$  and  $\text{R}^-$  ions. The anions of such *colloidal electrolytes* are so large that they cannot pass through membranes such as parchment paper. The sodium ion, however, can diffuse through, but the diffusion can proceed only to a slight extent before it is offset by the large electrostatic attraction, because of the creation of unbalanced positive and negative charges on each side of the membrane. When sodium chloride is present, however, the  $\text{Na}^+$  and  $\text{Cl}^-$  ions can diffuse through in pairs without upsetting the electrical equilibrium. When a mixture of congo red and sodium chloride is placed on one side of a membrane and sodium chloride alone on the other side and time is allowed for the attainment of equilibrium, it is found that the concentration of the  $\text{R}^-$  ion remains the same, but the total concentration of ions is greater on the congo-red side. The quantitative relations between the concentrations of the various ions and the osmotic effects have been developed by Donnan (originally also by Willard Gibbs) and checked by experiment. These relations can be described with the help of Fig. 80 where the ions  $\text{Na}^+$  and  $\text{R}^-$  at concentrations  $c_1$  are placed on one side *A* of a membrane permeable to water and to all ions except the colloidal  $\text{R}^-$  ions.

On the other side, *B*, of the membrane, sodium chloride is placed at concentration  $c_2$ .

It is assumed that both salts are practically completely dissociated. The  $\text{R}^-$  ions cannot diffuse through the membrane and their concentration remains constant at  $c_1$ , but the other three ions are free to

\* Langmuir, "Recent Advances in Surface Chemistry and Chemical Physics," page 1, Am. Assoc. Adv. Sci., The Science Press, New York, 1939; *Science*, **84**, 379 (1936).

† Donnan, *Chem. Rev.*, **1**, 73 (1924).

diffuse and at equilibrium will have definite concentrations, determined by two restrictions. According to the first restriction, the number of positive ions and negative ions must be equal in a given solution, insuring electric neutrality.

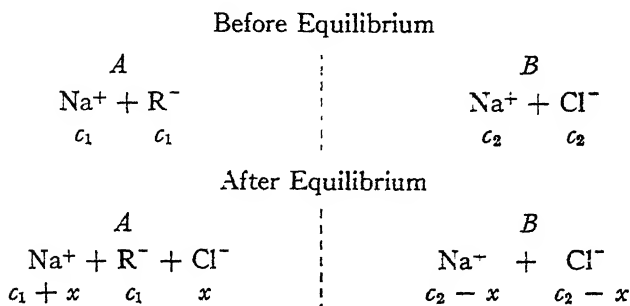


FIG. 80

According to the second restriction the product of the concentrations of sodium ions and chloride ions must be the same in solutions of sodium chloride which are at equilibrium. This principle will be discussed in a later chapter.

When equilibrium is reached,  $x$  ions of  $\text{Cl}^-$  and  $x$  ions of  $\text{Na}^+$  will have diffused into the compartment  $A$ , leaving  $c_2 - x$  ions of each in compartment  $B$ .

Then, since

$$(c_{\text{Na}^+} \times c_{\text{Cl}^-})_A = (c_{\text{Na}^+} \times c_{\text{Cl}^-})_B$$

$$x(c_1 + x) = (c_2 - x)(c_2 - x)$$

and therefore

$$\frac{x}{c_2} = \frac{c_2}{c_1 + 2c_2}$$

The term  $x/c_2$  gives the fraction of sodium chloride which diffuses through the membrane.

*Example 5.* In the membrane experiment just described, if the initial concentration of congo red in  $A$  is 10 (in arbitrary units) and that of sodium chloride in  $B$  is 20, what will be the concentration of each ion in each compartment after equilibrium is attained?

$$x = \frac{c_2^2}{c_1 + 2c_2} = \frac{400}{10 + 40} = 8$$

Then at equilibrium; in  $A$ ,  $c_{\text{Na}^+} = 18$ ,  $c_{\text{R}^-} = 10$  and  $c_{\text{Cl}^-} = 8$ ; and in  $B$ ,  $c_{\text{Na}^+} = 12$  and  $c_{\text{Cl}^-} = 12$ .

It is clear that the two restrictions mentioned above are met:  $18 = 10 + 8$  and  $12 = 12$ ; and  $18 \times 8 = 12 \times 12$ .

The Donnan membrane equilibrium finds several applications especially in the field of biology. It is particularly applicable to proteins and the lyophilic colloids. It explains the observed differences in concentration and the swelling of gelatin. Since the total concentration of solutes is greater on the side of a membrane containing ionizable colloids, it is clear that the vapor pressure will be less and there will be diffusion of water into the solution of greater concentration.

The interaction of slow and rapidly moving charged particles involves a Donnan effect just as if the particles and ions were separated by a membrane instead of by a difference in velocities. The Donnan effect may be suppressed by the addition of an excess of neutral electrolytes which diminish the zeta potential. In this way it is possible to obtain measurements in the sedimentation of proteins which are characteristic of the protein itself rather than of the assembly of protein-stabilizing ions. In the diffusion of dyes and particularly in the diffusion of the rapidly moving hydrogen ions it is necessary to allow for this Donnan effect or eliminate it with an excess of electrolyte. This salt effect introduces errors, however, in experiments on osmotic pressure described on page 242.

**Emulsions.** A dispersion of small drops of one liquid in another is known as an *emulsion*. Two liquids which are mutually insoluble may be emulsified by prolonged mechanical agitation, but if the resulting emulsion contains much more than 1 per cent of the disperse phase, it is unstable, and the component liquids soon separate into two layers. For example, a small portion of benzene in a large volume of water may be emulsified by shaking but, on standing, the small droplets of benzene soon coalesce and the liquids separate into two layers. The larger the proportion of benzene in the mixture, the more unstable the emulsion becomes. The addition of a third substance known as an *emulsifying agent*, or *emulsifier* stabilizes an emulsion. Thus, if a small amount of sodium oleate is dissolved in water and this solution is vigorously shaken with benzene, a stable emulsion will result. Emulsions of kerosene in water, containing as much as 99 per cent of oil in a 1 per cent soap solution, have been prepared and studied by Pickering. The emulsion containing 99 per cent of kerosene was found to resemble a solid. It frequently happens that a small amount of unsuspected impurity functions as an emulsifying agent.

Two main types of emulsion are recognized: (1) emulsions in which

oil is dispersed in water, known as the *oil-water* type; and (2) emulsions in which water is dispersed in oil, known as the *water-oil* type. The word "oil" is here used to designate any liquid which is insoluble in water. Of these two types of emulsion, the first is by far the more common.

Although the alkali soaps are excellent emulsifying agents for emulsions of the first type, it has been found that they are not satisfactory for emulsions of the second type. On the other hand, the soaps of the heavy metals are insoluble in water but they are effective in producing water in oil emulsions. Gum arabic, gelatin, agar-agar, albumin, and all the so-called solvated colloids are also good emulsifying agents.

Although it is often difficult to decide from a superficial examination whether an emulsion is of the oil-water or water-oil type, the question may be answered definitely by placing a few drops of the emulsion under a microscope and stirring in successively a little of one phase, and then a little of the other. The liquid of which the external phase is composed mixes readily with the emulsion; the other does not.

The preparation of stable emulsions is of great practical importance in pharmacy, in cooking, and in many industrial operations. Mechanical homogenizers are arranged to mix intimately two immiscible liquids by producing very fine droplets of one in the other. The cleansing action of ordinary soap depends in large measure on its ability to produce an emulsion of oil in water. The large surface of the emulsion droplets is effective in removing dirt and grease. One of the most important processes now used in mining operations for concentrating the valuable part of an ore is that of ore flotation. It is a process by which an oil emulsion and foam are produced and the mineral particles rise to the surface where the material is concentrated.

The reverse process of breaking up emulsions, known as "de-emulsification," is also of considerable practical importance. For example, petroleum frequently contains large amounts of emulsified water which is very difficult to remove. Several methods are available for de-emulsification; among these may be mentioned the Cottrell process, which employs a high-voltage precipitator, and methods based upon filtration, freezing out, and centrifugal separation. The last method is extensively used in dairies for separating cream.

Numerous theories have been advanced in explanation of the phenomena of emulsification. An important function of the emulsifying agent is its power to lower the interfacial tension between the



two liquids forming the emulsion. In an emulsion of benzene and water, the interfacial tension is approximately 35 dynes per centimeter, but the interfacial tension may be reduced to about 2 dynes per centimeter by the addition of sodium oleate.

Bancroft\* holds that the type of emulsion is determined by the phase which is the best solvent for the emulsifying agent. He suggests, for example, that if the adsorption of the emulsifying agent lowers the surface tension on the water side of the interface more than it does on the oil side, the interface will tend to curve around the oil droplets and will tend to emulsify oil in water.

According to another theory proposed by Hildebrand the most effective emulsifying agents are those whose molecules consist of long chains of carbon atoms with a strong polar group, such as the carboxyl group, at one end. The nonpolar end of the molecule is assumed to direct itself toward the oily liquid, whereas the polar end tends to enter the aqueous phase. If the nonpolar ends of the molecules can pack together more closely than the polar ends, the interfacial film will be bent toward the oil, and an emulsion of oil in water will result. This is commonly known as the *oriented wedge* hypothesis of emulsification.

**Gels.** When the conditions within a solution are so modified as to depress the solubility of the solute below a certain definite value, precipitation may occur, and the resulting precipitate may be crystalline or amorphous in character, depending on the time taken to precipitate and on other factors. Von Weimarn has shown that the degree of supersaturation, at the time of formation, and the viscosity of the medium account, qualitatively at least, for the observed phenomena. For example, when barium sulfate is precipitated from very dilute solutions it is possible to obtain small crystals. When the solutions are more concentrated the state of supersaturation after mixing is greater and the crystals become less pronounced. When the solutions contain about one equivalent per liter an immediate precipitate is formed which is apparently amorphous. With still more concentrated solutions (3 to 7 equivalents per liter of barium thiocyanate and manganese sulfate) a clear jelly is produced.

It is obvious then that we should not speak of crystalloidal and colloidal matter but rather of the crystalloidal and colloidal states. In fact, it is now recognized that it is simply a matter of overcoming experimental difficulties before it will be possible to obtain all forms of matter in the colloidal state.

\* Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., New York, 1932, page 261.

When a precipitate retains an appreciable quantity of the liquid in which it was dissolved in the form of a semi-rigid mass it is termed a "gelatinous precipitate," and if all the liquid is initially retained a jelly or *gel* is produced.

The production of gels by the cooling of a fluid colloidal solution or sol is one of the simplest and most familiar methods. As an example of this method, we may cite the formation of a typical gel by cooling to room temperature a 2 per cent gelatin sol in hot water. The resulting gel will be found to be stiff and transparent. It seems probable that, when such a sol cools, the molecular aggregates unite to form long filaments which interlace and give rise to a structure resembling a heap of brushwood.

Gels may be produced also by metathesis, as when an acid is mixed with sodium silicate in suitable concentrations. In concentrated solutions the resulting silicic acid forms a stiff, transparent gel immediately, but in very dilute solutions the completion of the gel may be delayed for fully a month.

A gel may be formed by changing the solvent as, for example, when chloroform is added to a nitrocellulose sol in amyl acetate. Coagulation occurs, and a transparent, viscous gel is obtained. It is of interest to note that, when the gel is pressed between the fingers, it is possible to remove nearly all the liquid, leaving a mass of cotton-like fiber in the hand. Apparently the greater part of the liquid is retained by the capillary action of the fibers.

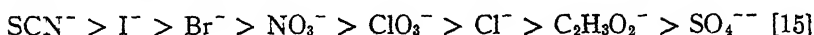
On standing, gels frequently undergo an appreciable shrinkage in volume with a simultaneous extrusion of liquid. This phenomenon is called *syneresis*. When placed in a dry atmosphere gels quickly dry out, and when placed in water they take up water, rapidly at first, and then more slowly. The rate depends on the difference between the weight of water which the gel holds and the maximum amount which it can hold. When placed in a salt solution, the salt distributes itself between the solvent and the gel, the rate of distribution varying greatly with the different ions.

The change of sol to gel is a reversible one in the case of gelatin. The gel is readily reconverted into a sol on warming the stiff gel obtained when a moderately concentrated solution of the gelatin is cooled. In albumin and certain other lyophilic colloids, however, a chemical change accompanies the heating and irreversible coagulation occurs, as exemplified in the boiling of an egg.

The behavior of gels on freezing depends largely on the amount of unadsorbed water, and this relation is important in explaining the winter hardness of certain types of seeds.

A surprisingly large number of common things of importance are gels, including soap, wood, resins, Bakelite, certain animal tissues, and rubber.

**Lyotropic Series.** Salts have a marked effect on the temperature of the gel-sol transformation, some tending to raise the temperature of gelation and others to lower it. The effect is not to be explained on the basis of ionic charge, and, in fact, univalent ions give widely different results. Hofmeister arranged the negative ions of sodium salts in the following order, the first having the greatest influence in lowering the temperature of gelation and the last one the least influence.



The same sequence of ions is maintained, not only in the gelation temperature of agar-agar and similar substances, but also in their rate of swelling, and the series finds applications in several different fields. The behavior of this series is not fully explained as yet, but it is related in some way to the diameter of the ion and the interaction between the ion and the dipoles of the water molecules.

**Industrial Colloids.** In addition to the suspension and emulsion colloids already described, there are a great many others of practical importance. Foams consist of air bubbles surrounded by liquid films, and these become troublesome in certain industrial processes of evaporation.

Clouds and smokes are colloid particles of liquids or solids dispersed in the gas phase. They tend to obscure vision and produce dirt in cities; sometimes they are responsible for large financial losses in chemical operations, and again they may constitute health hazards to animals and plants. A successful method of electrical precipitation, invented by Cottrell, is extensively used in smelting and other industries where a valuable or an objectionable dust or smoke passes out the chimney. A direct current at about 50,000 volts is passed from a central wire to the surrounding circular metal wall in the form of a corona discharge. The particles acquire electrical charges by attaching ions in the discharge and are quickly drawn to the electrodes from which they can then be scraped mechanically.

Proteins, dyes, and soaps constitute a group of colloids of known chemical structure. They are among the smallest colloid particles, and in fact the difference here between true solution and colloid solution is not sharply defined. These materials frequently dissociate into ions and are called colloidal electrolytes.

Another great group of colloid substances comprises the organic colloids such as cellulose, and its derivatives, carbohydrates, resins,

and rubber. The best use of these substances demands a knowledge of the principles of colloid chemistry.

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## PROBLEMS

1. Assuming that, in a colloidal solution of silver, each particle is a cube  $0.04\mu$  on an edge with a density of 10.5, (a) how many colloid particles can be produced from 0.1 g. of silver; (b) what is the total area of the silver particles; (c) what is the area of a single cube of silver weighing 0.1 g.?

*Ans.*  $1.49 \times 10^{14}$  particles. (b)  $1.43 \times 10^4 \text{ cm.}^2$  (c)  $0.268 \text{ cm.}^2$

2. Using the following modification of Stokes' law

$$\mu = \frac{2gr^2(S - S_0)}{9\eta}$$

where  $\mu$  = velocity

$g$  = force of gravity

$r$  = radius of particle

$S$  = density of particle

$S_0$  = density of medium

$\eta$  = viscosity of medium

calculate the time necessary for a quartz particle  $10\mu$  in diameter to fall 50 cm. in distilled water at room temperature.  $S = 2.6$ ;  $\eta_{\text{w}} = 0.0100$  poise.

*Ans.* 95.6 minutes.

3. A gold sol has particles of radius  $13 \text{ \AA}$ . Calculate the specific diffusion constant in water at  $20^\circ$  ( $\eta = 0.0100$  poise). *Ans.*  $1.64 \times 10^{-8}$ .

4. Magnesium oxide adsorbs silica from water and follows the Freundlich equation. It may be used to reduce boiler scale of silica. Plot the following data on log-log paper and calculate the constants of the Freundlich equation. Calculate

the parts per million of magnesium oxide needed to reduce the residual silica to 2.9 parts per million. (1 p.p.m. = 1 mg. per 1000 g.  $\text{H}_2\text{O}$ .)

MgO (ppm.)	0	75	100	200
Residual $\text{SiO}_2$ (p.p.m.)	26.2	9.2	6.2	1.0
$\text{SiO}_2$ removed (p.p.m.)	0	17.0	20.0	25.2

*Ans.* 153 p.p.m. MgO.

5. One cubic centimeter of a certain activated charcoal has a surface area of 1000 sq. meters. Assuming, as a limiting case, complete surface coverage, how much ammonia, at standard conditions, could be adsorbed on the surface of 45 ml. of activated charcoal? The diameter of the  $\text{NH}_3$  molecule is  $3 \times 10^{-8}$  cm., and it is assumed that the molecules just touch each other in a plane. *Ans.* 18.5 liters.

6. A mercury sol is composed of globules having a diameter of  $0.04\mu$ . What is the surface of the particles formed from 1 g. of mercury?

7. A solution containing 0.00143 g. of  $\text{Fe}_2\text{O}_3$  per ml. was diluted 1 part to 10,000. Ultramicroscopic count on the dilute solution gave an average of 3.12 particles per count in a field of view of 0.04 mm. diameter and 0.04 mm. depth. Assuming the density of the particle to be 5.2, and that the particles are spheres, what is the diameter of the particles?

8. A liter of 0.01  $M$  gelatin chloride " $G$ "Cl is placed on one side of a membrane and a liter of 0.1  $M$  sodium chloride is placed on the other. After equilibrium is reached what will be the concentration of sodium ion and chloride ion on each side of the membrane? The membrane is permeable to sodium ions and chloride ions but not to gelatin ions.

9. The adsorption of  $\text{N}_2$  on mica is as follows:

$p$	2.8	6.1	17.3	23.8
$x/m$	12	19	28.2	30.8

( $p$  is given in dynes per square centimeter and  $x/m$  is the cubic millimeters of gas at  $20^\circ$  and 760 mm. adsorbed on 24.3 g. of mica, having a surface of 5750 sq. cm.) Determine the constants of Freundlich's equation and calculate the value of  $x/m$  when  $p = 34$ . (The experimental value of  $x/m = 33$ .)

10. Show that Langmuir's equation may be written in the form  $p/y = 1/ab + p/b$ , where  $y = x/m$ . The constants  $a$  and  $b$  may be determined from the data of Problem 9 by plotting  $p/y$  against  $p$ . The straight line thus obtained has a slope  $1/b$  and an intercept  $1/ab$ . What are the values of the constants, and what is the calculated value of  $y$  when  $p = 34$  dynes per sq. cm.?

11. What is the osmotic pressure in millimeters at  $25^\circ$  of a 0.2 per cent colloidal solution of gold if the particles are cubical and  $30 \text{ \AA}$  on an edge?

12. Using the formula  $\mu = \frac{2gr^2(S - S_0)}{9\eta}$  (see Problem 2) calculate the time

necessary for a spherical calcium chloride particle  $40\mu$  in diameter to fall 1 in. in carbon tetrachloride at room temperature. ( $S_0 = 1.595$ ;  $S = 2.152$ ;  $\eta = 0.00975$  poise.)

13. The number of spherical particles in a given volume of mercury sol which had come to equilibrium in a gravitational field was 386 at one level and 193 at a level 0.10 mm. higher. The temperature was  $20^\circ$ . The specific gravity of mercury is 13.6, and that of the sol may be assumed to be 1. What is the average diameter of the particles?

14. Colloidal egg albumin has a particle weight of 40,500. What is the osmotic pressure at  $0^\circ$  of a solution containing 2 g. per liter?

15. The diameter of the hydrogen molecule is  $2.74 \text{ \AA}$ . If an adsorbent has a surface of 850 sq. meters per ml. and 95 per cent of the surface is active, how much  $\text{H}_2$  (measured at standard conditions) could be adsorbed by 50 ml. of the adsorbent? Assume that the adsorbed molecules just touch in a plane.

16. Ten grams of oleic acid ( $\text{C}_{17}\text{H}_{33}\text{COOH}$ ) is poured on the surface of a clean lake where the spreading film can be seen if the water is rippled by a gentle wind or marked with rain drops. The cross section of the molecule is about  $22 \text{ \AA}^2$ . What will be the maximum diameter in feet of a circular pool produced in this way?

17. From the Langmuir equation show that  $y$  is a linear function of  $p$  at very low pressures, and independent of  $p$  at very high pressures, and that the curves of the equation will approximate roughly in general shape the Freundlich adsorption isotherm.

18. When a given volume of olive oil was dropped through a standard tip into a 0.001  $M$  NaOH solution 44 drops were formed and the interfacial tension between olive oil and 0.001  $M$  NaOH was computed to be 7.3 dynes per cm. When the same volume of olive oil was dropped through the same standard tip into an aqueous solution 0.001  $M$  in NaOH and 0.15  $M$  in NaCl, 300 drops were formed. Calculate the interfacial tension between olive oil and an aqueous solution 0.001  $M$  in NaOH and 0.15  $M$  in NaCl.

19. Two solids I and II suspended in water are agitated with an agent which causes a froth to appear on the surface. Which solid would collect on the surface of the bubble films and which solid would stay suspended in the solution if

$$\gamma_{\text{air, soln.}} > \gamma_{\text{I, soln.}} + \gamma_{\text{I, air}}$$

and

$$\gamma_{\text{II, air}} > \gamma_{\text{air, soln.}} + \gamma_{\text{II, soln.}}$$

where the  $\gamma$ 's represent the interfacial tension between the phases indicated? The system will adjust so as to have the smallest free energy. The interfaces formed will be those which have the lowest interfacial tension.

20. The concentration  $c$  of colloid particles in a sedimentation equilibrium can be calculated from a standard differential equation

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} - v \frac{dc}{dx} = 0$$

where  $x$  is linear distance and  $D$  and  $v$  are constants. This equation finds many applications in the flow of matter and heat. Its general solution is  $c = ae^{vz/D} + b$ . Show that it can be used to derive equation (3).

21. In a centrifuge experiment with egg albumin in a buffered aqueous solution at a pH of 6, the boundary moved 6.3 cm. in 105 minutes as determined by direct measurement of the change in position of the photometer curves with time. The speed of the centrifuge was 57,000 rpm. The distance from the center of rotation was 6.43 cm. Show that the specific sedimentation constant for this material is  $3.5 \times 10^{-13}$  cm. per sec. per unit field, after multiplying by 0.81 to correct for density and viscosity.

22. Derive equation (8) for a state of equilibrium by setting the force of gravity acting downwards exactly equal to the force of diffusion acting upwards. Thus

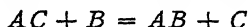
$$f_{\text{gravity}} = v S - S_0 g n \, dx, \text{ and } f_{\text{diffusion}} = \frac{-\partial p}{\partial x} dx \text{ where } p = (n/N)RT.$$

## CHAPTER XII

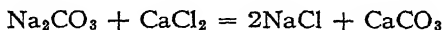
### CHEMICAL EQUILIBRIA

**Historical Introduction.** The nature of chemical affinity has been under discussion ever since the metaphysical speculations of the Greeks, who endowed the atoms with the instincts of love and hate. Newton's discovery of the law of gravitation led him to speculate on the nature of the force which attracts atoms.

Geoffroy and Bergmann arranged chemical substances in the order of their displacing power. Thus, if we have three substances, *A*, *B*, and *C*, and the attraction between *A* and *B* is greater than that between *A* and *C*, then, when *B* is added to *AC*, it will completely displace *C*, as indicated by the following equation:

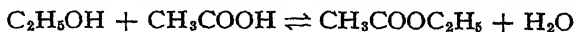


These investigators overlooked a factor of fundamental importance in conditioning chemical reactivity, namely, the influence of concentration. The importance of the relative amounts of the reacting substances in determining the course of a reaction was first clearly recognized by Wenzel, in 1777. It remained for Berthollet, however, to point out the significance of the views advanced by Wenzel. His first paper on this subject was published in 1799, while he was acting as a scientific adviser to Napoleon in Egypt. Under ordinary conditions, sodium carbonate and calcium chloride react according to the equation



This reaction proceeds nearly to completion. Berthollet observed the deposits of sodium carbonate on the shores of certain saline lakes and pointed out that this salt is produced by the reversal of the above reaction, the high concentration of sodium chloride in the water of the lakes causing the reaction to yield some sodium carbonate.

In 1862, Berthelot and Péan de St. Gilles investigated the reaction between ethyl alcohol and acetic acid represented by the equation



Starting with equivalent quantities of alcohol and acid, the reaction proceeds until about two-thirds of the reacting substances have been

converted into ester and water. In like manner, if equivalent quantities of ethyl acetate and water are brought together, the reaction proceeds in the direction indicated by the lower arrow, until about one-third of the original substances have been converted into acid and alcohol. In other words, the reaction is reversible, a condition of equilibrium resulting when the speeds of the two reactions, indicated by the upper and lower arrows, become equal. If a fixed amount of acid is taken, and the quantity of alcohol is varied, a corresponding displacement of the equilibrium results. The results, obtained by Berthelot and St. Gilles, for ethyl alcohol and 1 mole of acetic acid are shown in Table I. The first and third columns give the number of moles of alcohol added to 1 mole of acetic acid, and the second and fourth columns give the percentage of acetic acid converted into ester.

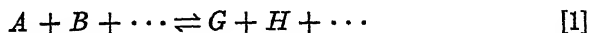
TABLE I  
INFLUENCE OF CONCENTRATION ON EXTENT OF REACTION

Moles of Alcohol	Per Cent Acid Converted	Moles of Alcohol	Per Cent Acid Converted
0.2	19.3	2.0	82.8
0.5	42.0	4.0	88.2
1.0	66.5	12.0	93.2
1.5	77.9	50.0	99.4

The effect on the course of the reaction is clearly due to an increase in the concentration of alcohol.

**The Law of Mass Action.** In 1867, Guldberg and Waage, two Scandinavian investigators, enunciated the law of mass action as follows: *The rate of a chemical reaction is proportional to the active masses of the reacting substances present at that time.* Guldberg and Waage defined the term "active mass" as the molecular concentration of the reacting substances. It is to be carefully noted that the amount of chemical action is not proportional to the actual quantities of the substances present, but rather to the amounts present in unit volume, i.e., to concentrations.

In general a reversible reaction like that between alcohol and acetic acid may be written



and the concentrations,  $c$ , of each constituent may be written  $c_A$ ,  $c_B$ ,  $c_G$ ,  $c_H$ . According to the mass law, the speed with which  $A$  and  $B$



react depends on the concentrations of  $A$  and  $B$ . Then

$$\text{Rate}_{\text{forward reaction}} \propto c_A c_B, \quad \text{or} \quad \text{Rate}_{\text{forward reaction}} = k_1 c_A c_B$$

where  $k_1$  is the specific rate constant. The rate is greatest when  $A$  and  $B$  are first mixed together, and it gradually decreases as these reactants are used up.

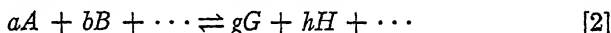
The products of the reaction,  $G$  and  $H$ , react to give  $A$  and  $B$ , and the rate of this reaction also depends on the concentration of  $G$  and  $H$ . Then

$$\text{Rate}_{\text{reverse reaction}} = k_2 c_G c_H$$

When more than 1 mole of a single substance is involved in the equation of a reaction, the number of moles must be considered in the mass law because the reaction rate depends on the number of collisions. Thus if the reaction involves  $2A + 1B$  the rate expression is

$$\text{Rate} = k_1 c_A^2 c_B$$

In the more general equation, each of the substances in the equation has a coefficient, 1, 2, or 3, etc. and equation (1) may be rewritten



showing that  $a$  moles of  $A$  and  $b$  moles of  $B$  react to give  $g$  moles of  $G$  and  $h$  moles of  $H$ . At equilibrium

$$\text{Rate}_{\text{forward reaction}} = \text{Rate}_{\text{reverse reaction}}$$

$$k_1 c_A^a c_B^b \cdots = k_2 c_G^g c_H^h \cdots$$

and

$$\frac{c_G^g c_H^h \cdots}{c_A^a c_B^b \cdots} = \frac{k_1}{k_2} = K_e \quad [3]$$

where  $K_e$  is a constant defined as the equilibrium constant expressed in concentrations. Concentrations are usually given in moles per liter. A more rigorous derivation for the equilibrium constant is given by means of thermodynamics on page 289. It can be shown that equations (3) and (4) (given below) are strictly true only for ideal, dilute solutions and perfect gases.

**Equilibrium Constants.** Since, at any one temperature, the partial pressure,  $p$ , of a perfect gas is proportional to its concentration,  $c$ , in the gas phase, we may write equation (3) in the following manner:

$$K_p = \frac{p_G^g p_H^h \cdots}{p_A^a p_B^b \cdots} \quad [4]$$

where  $K_p$  is the equilibrium constant expressed in partial pressures. Unless otherwise specified, the pressures are given in atmospheres.

In gaseous equilibria,  $K_p$  is used more often than  $K_c$ . The relation between the two equilibrium constants,  $K_c$  and  $K_p$ , can be determined easily since  $c = 1/v = p/RT$  and equation (5) is obtained by substituting this value of  $c$  into equation (3)

$$K_c = \frac{\left(\frac{p_G}{RT}\right)^g \left(\frac{p_H}{RT}\right)^h}{\left(\frac{p_A}{RT}\right)^a \left(\frac{p_B}{RT}\right)^b} = \left(\frac{1}{RT}\right)^{(g+h)-(a+b)} \frac{p_G^g \times p_H^h}{p_A^a \times p_B^b} = (RT)^{(a+b)-(g+h)} K_p \quad [5]$$

Letting  $\Delta n$  equal the change in the number of moles of gas during the reaction, i.e.,  $(g + h) - (a + b)$

$$K_p = K_c(RT)^{\Delta n} \quad [6]$$

In reactions where the same number of moles of gas occur on both sides of the equation,  $\Delta n = 0$  and  $K_c = K_p$ . Since concentrations are expressed in moles per liter and partial pressures in atmospheres, it is evident that the gas constant  $R$  must be expressed in liter-atmospheres.

*Example 1.* For the reaction  $N_2 + 3H_2 = 2NH_3$ , at  $400^\circ$

$$K_c = \frac{c_{NH_3}^2}{c_{N_2} \times c_{H_2}^3} = 0.507$$

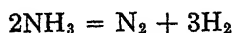
Calculate  $K_p$

$$K_p = (RT)^{\Delta n} K_c = (0.08205 \times 673.1)^{-2} \times 0.507 = 1.66 \times 10^{-4}$$

A large value of  $K_p$  means that the numerator is greater than the denominator, and a small value means that it is smaller. In this reaction the ammonia concentration at equilibrium is high when  $K_p$  is large, and it is low when  $K_p$  is small. The magnitude of the equilibrium constant is a measure of the extent to which the materials react to give the products, i.e., a measure of chemical affinity.

Certain conventions are observed in the use of equilibrium constants to avoid confusion. The equation for the reaction is always written down and the products at the right of the equality sign are placed in the numerator.

When the equation for the reaction is reversed, the new equilibrium constant becomes the reciprocal of the other. For example,



$$K_c = \frac{c_{N_2} \times c_{H_2}^3}{c_{NH_3}^2} = \frac{1}{0.507} = 1.97$$

If the reaction is written

$$\text{NH}_3 = \frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2$$

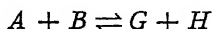
$$K_c = \frac{\sqrt{c_{\text{N}_2}} \sqrt{c_{\text{H}_2}^3}}{c_{\text{NH}_3}} = \sqrt{1.97} = 1.40$$

These fractional exponents are usually avoided by multiplying through by an appropriate integer.

**Determination of Equilibrium Constants.** Many chemical and physical measurements can be used in the determination of equilibrium constants. A considerable amount of ingenuity is often needed, not only in devising methods for analyzing the mixture without disturbing the equilibrium but also in calculating the concentration of all the substances present from an experimental determination of only one or two.

If there is a change in pressure or in volume during the reaction the composition at equilibrium can be calculated readily as shown in the following section. Other physical properties, such as absorption of light, or refractive index or electrical conductance, can be used in special cases to determine the concentration of one or more of the substances at equilibrium. Frequently chemical methods can be used, but if they involve a different temperature it is necessary to "freeze" the equilibrium mixture in some way so that it will not shift during the analysis. Sudden chilling or addition of an excess of some chemical reagent or removal of a catalyst is often effective for this purpose.

Usually the original concentrations of the reactants are known, and their concentrations at equilibrium are determined directly or they are calculated indirectly from the concentration of the products of equilibrium. For example, in the reaction



if 1 mole of *A* and 1 mole of *B* are mixed in a volume of 1 liter and allowed to come to equilibrium and if 0.9 mole per liter of *G* is found by analysis, it follows that the concentration of *H* must equal that of *G*, and the concentration of *A* and of *B* at equilibrium must be 1 - 0.9 or 0.1. The equilibrium constant then is written

$$K_c = \frac{c_G \times c_H}{c_A \times c_B} = \frac{0.9 \times 0.9}{0.1 \times 0.1} = 81$$

It is essential to know that equilibrium has been reached before the analysis of the mixture can be used for calculating the equilibrium constant. Sometimes the reaction is very slow and the mixture may

be far from equilibrium even though it does not appear to change. The following may serve as criteria for the attainment of equilibrium.

(1) The same equilibrium constant is obtained when the equilibrium is approached from both sides. In the example given the same value is obtained for  $K$  when  $A$  and  $B$  are mixed as when  $G$  and  $H$  are mixed.

(2) The same equilibrium constant is obtained when the concentrations of reacting materials are varied over a wide range.

(3) When the mixture is allowed to stand for longer and longer periods a concentration is finally reached which does not change with further standing.

Flow methods are sometimes used for determining equilibrium constants. For example, known mixtures of nitrogen and hydrogen are forced through a heated chamber (containing a catalyst) and the issuing gas is passed quickly through a capillary tube to an absorption bottle where the ammonia is titrated. The partial pressures of all three gases can then be calculated. The gas is passed through at various rates of flow and the equilibrium constant is calculated when the passage through is so slow that making it still slower does not increase the concentration of ammonia. When equilibrium is established a longer period of time will not produce any further change in the concentrations.

**Dissociation of Gases.** The determination of the density of a gas provides one of the simplest methods for measuring quantitatively the extent to which the gas is dissociated. When a gas dissociates, more molecules are produced and at constant temperature and pressure, the volume increases. The density or the weight per liter then decreases, and the difference between the density of the undissociated gas and the partially dissociated gas permits a calculation of the degree of dissociation.

If we start with 1 mole of gas and let  $\alpha$  represent the fraction dissociated, then  $1 - \alpha$  will denote the fraction remaining undissociated. If 1 mole of gas yields  $\nu$  moles of gaseous products, the total number of moles present at any time will be

$$(1 - \alpha) + \nu\alpha \quad \text{or} \quad 1 + (\nu - 1)\alpha$$

Since the density of a given weight of gas at constant pressure is *inversely* proportional to the number of moles, the ratio of the density,  $d_1$ , of the undissociated gas to the density of the partially dissociated gas,  $d_2$  is given by the expression

$$\frac{d_1}{d_2} = \frac{1 + (\nu - 1)\alpha}{1} \quad [7]$$

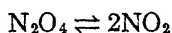
$$\alpha = \left( \frac{d_1}{d_2} - 1 \right) / (\nu - 1) = \frac{d_1 - d_2}{d_2(\nu - 1)} \quad [8]$$

It is always advantageous to visualize a formula if possible by checking it with some simple calculation. Referring to equation (8), if there is no dissociation  $\alpha = 0$  and  $d_1 = d_2$ ; if dissociation is complete,  $\alpha = 1$  and  $d_2(\nu - 1) = d_1 - d_2$  or  $d_1 = \nu d_2$ . Obviously both these relations are in agreement with the experimental facts.

Molecular weights may be substituted for densities, giving

$$\alpha = \frac{M_1 - M_2}{M_2(\nu - 1)} \quad [9]$$

where  $M_1$  is the molecular weight of the undissociated gas and  $M_2$  is the average molecular weight of the gases when the gas is partly dissociated. Densities are converted into molecular weights by multiplying the molar volume in liters at a given temperature by the weight of 1 liter. The use of formula (9) is illustrated in Table II with the reaction



in which  $\nu = 2$ .

TABLE II  
DENSITIES OF PARTIALLY DISSOCIATED NITROGEN TETROXIDE  
( $\text{N}_2\text{O}_4$ ) AT ONE ATMOSPHERE PRESSURE

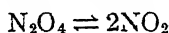
Temp. °C.	Average Molecular Weight Partially Dissociated Gas ( $M_2$ )	$\alpha = \frac{92.02 - M_2}{M_2}$
15	82.00	0.122
25	77.64	0.185
35	72.45	0.270
45	66.80	$x$
55	61.24	0.502
65	56.51	0.628
75	52.85	0.741

The mean molecular weight,  $M_2$ , of the partially dissociated gas is determined experimentally, and  $M_1$  is taken as the theoretical molecular weight of undissociated nitrogen tetroxide ( $\text{N}_2\text{O}_4$ ), i.e., 92.02. Here there is a simple quantitative check on the dissociation process, for the  $\text{NO}_2$  formed by dissociation is brown and the undissociated  $\text{N}_2\text{O}_4$  is colorless. It is easily noticed that the color becomes darker brown as the temperature is raised and the density becomes less. The color may be measured quantitatively with a colorimeter or photo-electric colorimeter.

*Example 2.* If 0.1588 g. of nitrogen tetroxide gives a total pressure of 760 mm. when partially dissociated in a 500-cc. glass vessel at 25°, what is the degree of dissociation  $\alpha$ ?

$$\begin{aligned}
 Pv &= \frac{g}{M} RT \\
 M_2 &= \frac{RT}{P} \frac{g}{v} = \frac{82.05 \times 298.1 \times 0.1588}{1 \times 500} \\
 &= 77.68 \\
 \alpha &= \frac{92.02 - 77.68}{77.68} = 0.1846
 \end{aligned}$$

**Equilibrium Constants in Gases.** The dissociation of nitrogen tetroxide is represented by the equation



and

$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} \quad [10]$$

If  $\alpha$  represents the degree of dissociation,  $(1 - \alpha)$  is proportional to the number of moles of undissociated  $\text{N}_2\text{O}_4$ ;  $2\alpha$  is proportional to the number of moles of  $\text{NO}_2$ ; and  $(1 - \alpha) + 2\alpha$  or  $1 + \alpha$  is proportional to the total number of moles.

If the total pressure is  $P$ , the partial pressures are as follows:

$$p_{\text{N}_2\text{O}_4} = \frac{1 - \alpha}{1 + \alpha} P \quad \text{and} \quad p_{\text{NO}_2} = \frac{2\alpha}{1 + \alpha} P$$

Then

$$K_p = \frac{\left( \frac{2\alpha}{1 + \alpha} P \right)^2}{\frac{1 - \alpha}{1 + \alpha} P} = \frac{4\alpha^2 P}{1 - \alpha^2} \quad [11]$$

In this reaction there is an increase in volume, 1 mole of gas dissociating into 2. According to the principle of Le Chatelier, it is possible to predict qualitatively that a decrease of pressure will cause the system to shift toward  $2\text{NO}_2$ , which occupies the larger volume. Equation (11) makes it possible to calculate quantitatively the degree of dissociation of  $\text{N}_2\text{O}_4$  at any pressure.

*Example 3.* At 25.0° and 1 atm., nitrogen tetroxide has been found by vapor density measurements to be 18.46 per cent dissociated. Find  $K_p$ .

$$K_p = \frac{4\alpha^2 P}{1 - \alpha^2} = \frac{4 \times (0.1846)^2}{1 - (0.1846)^2} \times 1 = 0.141$$

Calculate the degree of dissociation of nitrogen tetroxide at one-half an atmosphere and  $25^\circ$ .

$$K_p = 0.141 = \frac{4\alpha^2 (0.5)}{1 - \alpha^2}$$

and

$$0.141 (1 - \alpha^2) = 2\alpha^2$$

$$\alpha = 0.257$$

When phosphorus pentachloride is vaporized it dissociates according to the following equation



When 1 mole of  $\text{PCl}_5$  dissociates there will be at equilibrium  $1 - \alpha$  mole of  $\text{PCl}_5$ ,  $\alpha$  mole of  $\text{PCl}_3$ , and  $\alpha$  mole of  $\text{Cl}_2$ , where  $\alpha$  is the degree of dissociation. If these gases are contained at equilibrium in a vessel of  $v$  liters the concentrations in moles per liter are

$$c_{\text{PCl}_5} = \frac{1 - \alpha}{v}; \quad c_{\text{PCl}_3} = \frac{\alpha}{v}; \quad \text{and} \quad c_{\text{Cl}_2} = \frac{\alpha}{v}$$

The total number of moles is

$$[1 - \alpha] + \alpha + \alpha = 1 + \alpha$$

and the mole fractions are

$$N_{\text{PCl}_5} = \frac{1 - \alpha}{1 + \alpha}; \quad N_{\text{PCl}_3} = \frac{\alpha}{1 + \alpha}; \quad \text{and} \quad N_{\text{Cl}_2} = \frac{\alpha}{1 + \alpha}$$

If  $P$  is the total pressure the partial pressures are

$$p_{\text{PCl}_5} = \frac{1 - \alpha}{1 + \alpha} P; \quad p_{\text{PCl}_3} = \frac{\alpha}{1 + \alpha} P; \quad \text{and} \quad p_{\text{Cl}_2} = \frac{\alpha}{1 + \alpha} P$$

The equilibrium constant can be expressed in moles per liter ( $K_c$ ) in partial pressures ( $K_p$ ) or in mole fractions ( $K_N$ ) as follows:

$$K_c = \frac{c_{\text{PCl}_3} \times c_{\text{Cl}_2}}{c_{\text{PCl}_5}} = \frac{\frac{\alpha}{v} \times \frac{\alpha}{v}}{\frac{1 - \alpha}{v}} = \frac{\alpha^2}{(1 - \alpha)v} \quad [12]$$

$$K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{\frac{\alpha}{1 + \alpha} P \times \frac{\alpha}{1 + \alpha} P}{\frac{1 - \alpha}{1 + \alpha} P} = \frac{\alpha^2}{1 - \alpha^2} P \quad [13]$$

$$K_N = \frac{n_{\text{PCl}_3} n_{\text{Cl}_2}}{n_{\text{PCl}_5}} = \frac{\alpha^2}{1 - \alpha^2} n \quad [14]$$

where  $n$  is the total number of moles.

*Example 4.* At  $250^\circ$  one liter of partially dissociated phosphorus pentachloride gas, at 1 atm., weighs 2.695 g. Calculate the degree of dissociation  $\alpha$  from the measured density of the gas and calculate the equilibrium constant  $K_p$ . Starting with 1 mole of phosphorus pentachloride having a molecular weight of 208.3 there are  $1 + \alpha$  moles in the partially dissociated gas, and the density  $d$  is given by the expression

$$d = \frac{g}{v} = \frac{M}{1 + \alpha} \times \frac{P}{RT} \quad [15]$$

$$d = 2.695 = \frac{208.3 \times 1}{(1 + \alpha) 0.08205 \times 523.1}$$

$$\alpha = 0.80$$

According to equation (13)

$$K_p = \frac{0.80^2 \times 1}{1 - 0.80^2} = 1.78$$

This reaction is an interesting one to study in more detail. Qualitatively, it can be seen that increasing the total pressure will decrease the amount of dissociation because the undissociated gas occupies the smaller volume. If chlorine is added,  $p_{\text{Cl}_2}$  increases and, since  $K_p$  remains constant,  $p_{\text{PCl}_3}$  must diminish and  $p_{\text{PCl}_5}$  must increase. The degree of dissociation is decreased also by the addition of  $p_{\text{PCl}_3}$ . In general the dissociation of any substance is repressed by the addition of its dissociation products. The addition of an inert gas which takes no part in the reaction has no effect on the dissociation.

*Example 5.* What will be the degree of dissociation of phosphorus pentachloride when 0.1 mole at  $250^\circ$  is placed in a 3-liter vessel containing chlorine at one-half an atmosphere pressure? Let  $x$  = the additional number of moles of chlorine or phosphorus trichloride formed by the dissociation of the phosphorus pentachloride

$$K_p = 1.78 = \frac{p_{\text{PCl}_3} p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{\frac{x}{v} RT \left( \frac{1}{2} + \frac{x}{v} RT \right)}{\frac{(0.1 - x) RT}{v}} = \frac{x \left[ \frac{1}{2} + \frac{(0.08205)(523.1)x}{3} \right]}{0.1 - x}$$

$$x = 0.0574$$

The degree of dissociation =  $0.0574/0.1 = 0.574$ .



*Example 6.* How many moles of  $\text{PCl}_5$  must be added to a liter vessel at  $250^\circ$  in order to obtain a concentration of 0.1 mole of chlorine per liter?

$x$  = number of moles of  $\text{PCl}_5$  added to vessel

$$K_p = 1.78 = \frac{p_{\text{PCl}_3} p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{\left(0.1 \frac{RT}{v}\right) \left(0.1 \frac{RT}{v}\right)}{(x - 0.1) \frac{RT}{v}} = \frac{0.1^2}{(x - 0.1)} \times \frac{RT}{v}$$

$$= \frac{0.01 \times 0.08205 \times 523.1}{(x - 0.1)}$$

$$x = 0.341 \text{ mole}$$

*Example 7.* Under what total pressure must an equimolecular mixture of chlorine and phosphorus trichloride be placed in order to obtain 1 atm. of phosphorus pentachloride at  $250^\circ$ ? Letting  $x$  = the initial pressure of phosphorus trichloride or chlorine

$$K_p = 1.78 = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{(x - 1)(x - 1)}{1}$$

$$x = 2.33 \text{ atm.}$$

The total pressure at equilibrium is

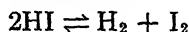
$$p_{\text{PCl}_3} + p_{\text{Cl}_2} + p_{\text{PCl}_5} = 1.33 + 1.33 + 1 = 3.66 \text{ atm.}$$

*Example 8.* Under what pressure must an equimolecular mixture of chlorine and phosphorus trichloride be placed at  $250^\circ$  in order to obtain an 80 per cent conversion of the phosphorus trichloride into phosphorus pentachloride?

$$K_p = 1.78 = \frac{\alpha^2}{1 - \alpha^2} P = \frac{0.20 \times 0.20}{1 - 0.20^2} P$$

$$P = 42.7 \text{ atm.}$$

Very careful measurements are available\* for the equilibrium



Quartz vessels of known volume were filled with hydriodic acid at a measured pressure and heated in an electrical thermostat to  $425.1^\circ$  for several hours until equilibrium was established. The vessels were then chilled quickly and analyzed for iodine by titration with sodium thiosulfate. The concentration of hydrogen at equilibrium is equal to that of the iodine. The concentration of hydriodic acid at equilibrium is obtained by subtracting the iodine from the initial hydriodic acid. The equilibrium concentrations in moles per liter are shown in Table III. The last three sets of data were obtained by starting from

\* Taylor and Crist, *J. Am. Chem. Soc.*, **63**, 1381 (1941).

the other side of the equilibrium, weighing initial quantity of iodine, measuring the pressure of hydrogen, and titrating the iodine after reaching equilibrium. The hydriodic acid concentration was determined by subtracting the final iodine concentration from the initial concentration. The close check between the two sets of data show that equilibrium was reached in every case.

TABLE III

EQUILIBRIUM BETWEEN HYDROGEN, IODINE AND HYDRIODIC ACID AT 698.6 K.

$c_{I_2}$ (mole/liter) $\times 10^3$	$c_{H_2}$ (mole/liter) $\times 10^3$	$c_{HI}$ (mole/liter) $\times 10^3$	$K = \frac{c_{H_2}c_{I_2}}{c_{HI}^2}$
1.7069	2.9070	16.482	1.827
1.2500	3.5600	15.588	1.831
0.7378	4.5647	13.544	1.835
2.3360	2.2523	16.850	1.853
3.1292	1.8313	17.671	1.835
0.4789	0.4789	3.531	1.840
1.1409	1.1409	8.410	1.840
0.4953	0.4953	3.655	1.832

Sometimes calculations are facilitated by expressing the concentrations with letters. Thus if  $a$  moles of hydrogen are mixed with  $b$  moles of iodine, and  $2x$  moles of hydriodic acid are formed, when equilibrium is established,  $a - x$  is the amount of hydrogen, and  $b - x$  is the amount of iodine present. Then substituting these quantities into the expression for the equilibrium constant

$$K_c = \frac{c_{H_2}c_{I_2}}{c_{HI}^2} = \frac{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)}{\left(\frac{2x}{v}\right)^2} = \frac{(a-x)(b-x)}{4x^2}$$

$$x = \frac{a+b - \sqrt{(a-b)^2 + 16abK_c}}{2(1-4K_c)} \quad [16]$$

It is of interest to note that a change in pressure does not alter the equilibrium in this gaseous reaction. Making use of the partial pressures of the components of the gaseous system, instead of the concentrations,

$$\frac{p_{H_2} \times p_{I_2}}{p_{HI}^2} = K_p$$

Now if the total pressure on the system is increased to  $n$  times its

original value. all the partial pressures are increased in the same proportion, and

$$\frac{n p_{\text{H}_2} \times n p_{\text{I}_2}}{n^2 p_{\text{HI}}^2} = K_p$$

which will be seen to be equivalent to the original expression, since  $n$  cancels out. The equilibrium is thus seen to be independent of the pressure. This independence applies only to those systems in which no change in volume occurs during the reaction. It will be remembered also that in this case  $K_p = K_c$ .

*Example 9.* The reaction  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  was investigated by passing mixtures of  $\text{CO}_2$  and  $\text{H}_2$  over a catalyst at  $900^\circ$ . The resulting gas was chilled quickly to room temperature by passage through a capillary and was analyzed. In one experiment the partial pressures were as follows:  $\text{CO}_2 = 0.2142$ ;  $\text{H}_2 = 0.2549$ ;  $\text{CO} = 0.2654$ ;  $\text{H}_2\text{O} = 0.2654$  atm. Calculate the number of moles of hydrogen present in an equilibrium mixture containing 22.72 moles of CO, 22.72 moles of  $\text{H}_2\text{O}$ , and 48.50 moles of  $\text{CO}_2$ .

$$K_p = \frac{p_{\text{CO}} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}} = \frac{0.2654 \times 0.2654}{0.2142 \times 0.2549} = 1.290$$

$$K_p = 1.290 = \frac{\left(22.72 \frac{RT}{v}\right) \left(22.72 \frac{RT}{v}\right)}{\left(48.50 \frac{RT}{v}\right) \left(x \frac{RT}{v}\right)}$$

$$x = \frac{22.72^2}{48.50 \times 1.290} = 8.25 \text{ moles H}_2$$

*Example 10.* When a mixture of 3 volumes of hydrogen and 1 volume of nitrogen is heated to  $400^\circ$  and subjected to 10 atm. in the presence of a suitable catalyst it is found that 3.85 per cent by volume (molar per cent) of the gaseous mixture is ammonia.

Calculate  $K_p$  for the reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ . The ratio of three volumes of  $\text{H}_2$  to 1 volume of nitrogen is maintained regardless of the amount of ammonia formed. Of the 96.15 per cent which is not ammonia  $\frac{1}{4}$  is nitrogen and  $\frac{3}{4}$  is hydrogen.

$$K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}^3} = \frac{(0.0385 \times 10)^2}{(\frac{1}{4} \times 0.9615 \times 10) (\frac{3}{4} \times 0.9615 \times 10)^3} = 0.000164$$

Calculate the total pressure  $P$  necessary to give a mixture containing 5 per cent ammonia at this temperature.

$$p_{\text{NH}_3} = 0.05P \quad p_{\text{N}_2} = \frac{1}{4} \times 0.95P \quad p_{\text{H}_2} = \frac{3}{4} \times 0.95P$$

$$K_p = 0.000164 = \frac{(0.05P)^2}{(0.2375P)(0.7125P)^3} = \frac{0.0025P^2}{0.0859P^4}$$

$$P^2 = \frac{0.0025}{0.000164 \times 0.0859} = 177.5 \quad P = 13.3 \text{ atm.}$$

Calculate the percentage of ammonia when the mixture is subjected to a pressure of 50 atm.

$$p_{H_2} = 3p_{N_2}, \quad p_{N_2} + p_{H_2} + p_{NH_3} = 50 \text{ atm.} \quad p_{NH_3} = 50 - 4p_{N_2}$$

$$K_p = 0.000164 = \frac{p_{NH_3}^2}{p_{N_2}p_{H_2}^3} = \frac{(50 - 4p_{N_2})^2}{(p_{N_2})(3p_{N_2})^3} = \frac{(50 - 4p_{N_2})^2}{27p_{N_2}^4}$$

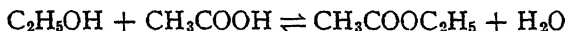
$$\frac{50 - 4p_{N_2}}{p_{N_2}^2} = \sqrt{0.000164 \times 27} = 6.65 \times 10^{-2}$$

$$p_{N_2} = 10.62, \quad p_{H_2} = 3 \times 10.62 = 31.86$$

$$p_{NH_3} = 50 - (10.62 + 31.86) = 7.52.$$

$$\text{Per cent ammonia} = \frac{7.52}{50.0} \times 100 = 15$$

**Equilibria in Liquid Systems.** The reaction between an alcohol and an acid, to form an ester and water, may be taken as an example of equilibrium in a liquid system. In the reaction



let  $a$ ,  $b$ ,  $c$ , and  $d$  represent the number of moles of alcohol, acid, ester, and water, respectively, which were initially present in  $v$  liters of the mixture, and let  $x$  denote the number of additional moles of ester and water which have been formed, when the system has reached equilibrium.

Neglecting the slight change in volume when the reaction takes place, the concentrations of the components will be,

$$c_{alc} = \frac{a - x}{v}; \quad c_{acid} = \frac{b - x}{v}; \quad c_{ester} = \frac{c + x}{v}; \quad \text{and} \quad c_{water} = \frac{d + x}{v}$$

Applying the law of mass action,

$$K_c = \frac{c_{ester}c_{water}}{c_{alc}c_{acid}} = \frac{(c + x)(d + x)}{(a - x)(b - x)} \quad [17]$$

This reaction, already mentioned, can now be studied more quantitatively. When equivalent amounts of alcohol and acid are mixed, the reaction proceeds until two-thirds of the mixture is changed into ester and water. Hence,

$$K_c = \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = 4 \quad [18]$$

The value of  $K_c$  having been determined, it may now be used to calculate the equilibrium conditions for any initial concentrations of the substances involved in the reaction. For example, if 1 mole of

glacial acetic acid is treated with varying amounts  $a$  of alcohol the amounts of ester and water  $x$  formed can be calculated easily. If there is no ester or water in the initial mixture the equation takes the form:

$$\frac{x^2}{(a-x)(1-x)} = 4$$

Solving

$$x = \frac{2}{3}(1 + a \mp \sqrt{a^2 - a + 1}) \quad [19]$$

A comparison of the observed and calculated values given in Table IV shows that the agreement is excellent, even in the more concentrated solutions where one might reasonably expect that the law of mass action in terms of concentrations would cease to hold.

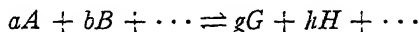
TABLE IV  
EQUILIBRIUM IN THE REACTION BETWEEN ACETIC ACID AND ALCOHOL

Alcohol, $a$ (moles)	Ester (observed), $x$ (moles)	Ester (calculated), $x$ (moles)
0.05	0.05	0.049
0.08	0.078	0.078
0.18	0.171	0.171
0.28	0.226	0.232
0.33	0.293	0.311
0.50	0.414	0.423
0.67	.....	$y$
1.0	0.665	0.667
2.24	0.876	0.864
8.0	0.966	0.945

In the equilibrium just studied the volume terms cancel out, and so the equilibrium constant is not affected by changing the volume. When there is a change in the number of molecules, however, it is necessary to consider the volume of the solution in calculating the equilibrium constant. Some solutions are sufficiently near to ideal solutions so that reliable constants can be obtained even at fairly high concentrations, but in solutions as concentrated as the ones just studied the calculated "constant"  $K$  may have different values at different concentrations. Better results are obtained in concentrated solutions by using mole fractions as given in equation (14).

**Free Energy Changes in Chemical Reactions.** A very important relation exists between the equilibrium constant and the change in free energy. It connects chemical reactivity with the measurements of thermodynamics and electrochemistry.

A general reaction may be written as before



and at equilibrium the partial pressures are  $p_A$ ,  $p_B$ ,  $p_G$ , and  $p_H$ . The reaction is imagined as occurring in a special equilibrium box shown in Fig. 81. It is imagined to be of infinite size so that the addition or subtraction of 1 mole of gas makes no appreciable difference in the pressure of the gas contained in it. Chambers containing the gases are connected with the box through hypothetical semi-permeable membranes, each of which is permeable to only one gas.

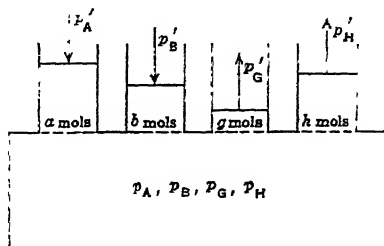


FIG. 81

The different gases in the separate chambers may have any pressures represented by  $p'_A$ ,  $p'_B$ ,  $p'_G$ , and  $p'_H$ . For the derivation of formula (4) it is necessary to assume that the gases are perfect gases.

The object of the following hypothetical operation is to determine how large a free energy change is involved in forcing the reacting materials into the box and forcing the products out.

In the first chamber,  $a$  moles of the gas  $A$  are compressed reversibly from pressure  $p'_A$  to pressure  $p_A$ , corresponding to the partial pressure of  $A$  in the equilibrium box. The increase in free energy  $\Delta F_1$  in this operation is given by equation (20).\*

$$\Delta F_1 = aRT \ln \frac{p_A}{p'_A} \quad [20]$$

The  $a$  moles of  $A$  at pressure  $p_A$  are then forced through the semi-permeable membrane into the equilibrium box by applying a pressure infinitesimally greater than  $p_A$ . This compression requires the expenditure of work equal to the pressure multiplied by the shrinkage in volume, but there is no change in the free energy of the gas because the pressure of each part of the system and the temperature are constant and the system is in equilibrium.

In the same way  $b$  moles of  $B$  are compressed reversibly from pressure  $p'_B$  to pressure  $p_B$  and forced through the second semi-permeable membrane into the large equilibrium box, and the free energy change

\* It may be imagined that during this operation the semi-permeable membrane is covered up.

$\Delta F_2$  is given by equation (21)

$$\Delta F_2 = bRT \ln \frac{p_B}{p'_B} \quad [21]$$

While  $a$  moles of  $A$  and  $b$  moles of  $B$  are being forced into the equilibrium box,  $g$  moles of  $G$  are removed by applying a pressure above the semi-permeable membrane infinitesimally less than  $p_G$ ; and  $h$  moles of  $H$  are removed at pressure  $p_H$ . In this way, equilibrium conditions are maintained at all times. When these gases are removed, they are then expanded or compressed to pressures  $p'_G$  and  $p'_H$ , respectively, the free energy changes being given by

$$\Delta F_3 = gRT \ln \frac{p'_G}{p_G} \quad [22]$$

and

$$\Delta F_4 = hRT \ln \frac{p'_H}{p_H} \quad [23]$$

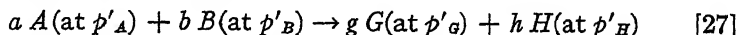
The total change in free energy is

$$\begin{aligned} \Delta F = \Delta F_1 + \Delta F_2 + \Delta F_3 + \Delta F_4 = aRT \ln \frac{p_A}{p'_A} + bRT \ln \frac{p_B}{p'_B} \\ + gRT \ln \frac{p'_G}{p_G} + hRT \ln \frac{p'_H}{p_H} \end{aligned} \quad [24]$$

$$\Delta F = RT \ln \left( \frac{p_A^a p_B^b p'_G{}^g p'_H{}^h}{p'_A{}^a p'_B{}^b p_G{}^g p_H{}^h} \right) \quad [25]$$

$$\Delta F = -RT \ln \frac{p_G{}^g \times p_H{}^h}{p_A{}^a \times p_B{}^b} + RT \ln \frac{p'_G{}^g \times p'_H{}^h}{p'_A{}^a \times p'_B{}^b} \quad [26]$$

The net result of this operation has been the reaction of  $a$  moles of  $A$  at a pressure  $p'_A$  with  $b$  moles of  $B$  at a pressure  $p'_B$  to give  $g$  moles of  $G$  at  $p'_G$  and  $h$  moles of  $H$  at  $p'_H$ , all at constant temperature  $T$ . The changes may be written briefly as



Equation (26) gives the change in free energy which accompanies this change in state at constant temperature, no matter how it is carried out, in terms of the pressures  $p'_A$ ,  $p'_B$ , etc., and a set of partial pressures  $p_A$ ,  $p_B$ , etc., for which the reaction is in equilibrium.

Using another equilibrium box with any other set of equilibrium partial pressures, say  $p^*_A$ ,  $p^*_B$ ,  $p^*_G$ , and  $p^*_H$ , the free energy for this

same change in state represented by (27) will be

$$\Delta F = -RT \ln \frac{p_{G'}^* p_{H'}^*}{p_{A'}^* p_{B'}^*} + RT \ln \frac{p_{G'}' p_{H'}'}{p_{A'}' p_{B'}'} \quad [28]$$

Since  $\Delta F$  in equation (26) is the same as in equation (28), we must have

$$\frac{p_{G'} \times p_{H'}}{p_{A'} p_{B'}} = \frac{p_{G'}^* p_{H'}^*}{p_{A'}^* p_{B'}^*} \quad [29]$$

In other words, at equilibrium at constant temperature this function of the pressures is a constant, and it is known as the equilibrium constant,  $K_p$ . This constitutes a thermodynamic proof of the validity of the equilibrium constant for perfect gases.

The quotient  $(p_{G'} \times p_{H'}) / (p_{A'} \times p_{B'})$  in the last term of equation (26) may be called the pressure quotient  $Q_p$ . It is of the same form as  $K_p$  but the pressures  $p'$  of the reacting materials and products are arbitrarily chosen and can have any values whatever. Then, introducing  $K_p$  and  $Q_p$  into equation (26)

$$\Delta F = -RT \ln K_p + RT \ln Q_p \quad [30]$$

This is an exceedingly important equation which will be applied to practical problems in later chapters. It gives the change in free energy which accompanies the chemical reaction in which  $a$  moles of  $A$  and  $b$  moles of  $B$  at any specified pressures are converted into  $g$  moles of  $G$  and  $h$  moles of  $H$  at any specified pressures.

There is a special case which is of importance — that in which the reactants in their standard states (1 atm. for gases) react to give the products in their standard states (1 atm.). The free energy change involved in these standard states is designated with a superscript zero,  $\Delta F^0$ , and is called the *standard* free energy change. Under these conditions the last term drops out because  $Q = 1$  and  $\log 1 = 0$ . Then

$$\Delta F^0 = -RT \ln K_p \quad [31]$$

The superscript zero indicates that the change in free energy refers to the reaction in which the reactants in their standard states, usually, at 1 atm., are converted into products in their standard states (at 1 atm.).

This important equation shows that the standard free energy decrease during a reaction is a measure of the magnitude of the equilibrium constant, i.e., of the chemical affinities involved. It determines just how far the reaction will go and what the partial pressures will be at equilibrium.



*Example 11.* For the reaction  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$  at  $25^\circ$

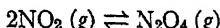
$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} = 0.141$$

What is  $\Delta F^0$  for the reaction?

$$\Delta F^0 = -RT \ln K_p = -1.987 \times 298.1 \times 2.303 \log 0.141 = +1161 \text{ cal.}$$

According to this calculation when 1 mole of  $\text{N}_2\text{O}_4$  at 1 atm. is converted into 2 moles of  $\text{NO}_2$  at 1 atm., 1161 cal. of free energy is required.

*Example 12.* What is  $\Delta F^0$  at  $25^\circ$  for the reaction



$$K_p = \frac{p_{\text{N}_2\text{O}_4}}{p_{\text{NO}_2}^2} = \frac{1}{0.141} = 7.09$$

$$\Delta F^0 = -RT \ln K_p = -1.987 \times 298.1 \times 2.303 \log 7.09 = -1161 \text{ cal.}$$

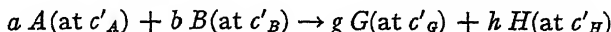
It is clear that if a reaction is reversed the equilibrium constant becomes the reciprocal of that for the forward reaction, and the free energy change has the same magnitude but the opposite sign.

*Example 13.* What is the free energy change involved at  $25^\circ$  if 10 g. of  $\text{N}_2\text{O}_4$  at 2 atm. is changed into 10 g. of  $\text{NO}_2$  at 0.3 atm.?

$$\begin{aligned} \Delta F &= -RT \ln K_p + RT \ln Q = -RT \ln K_p + RT \ln \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} \\ &= -1.987 \times 298.1 \times 2.303 \log 0.141 + 1.987 \times 298.1 \times 2.303 \log \frac{0.3^2}{2} \\ &= 1161 - 1837 = -676 \text{ cal.} \end{aligned}$$

This free energy change is for one mole of  $\text{N}_2\text{O}_4$  corresponding to the equation as written. The free energy change for 10 g. is  $\frac{10}{92.0} \times (-676) = -73.5 \text{ cal.}$

**Free Energy Changes in Solution.** Formulas similar to (26), (30), and (31) may be derived for ideal solutions. The free energy change in the case of dilute ideal solutions, for the isothermal change of state



is given by

$$\Delta F = -RT \ln \frac{c_G^g c_H^h}{c_A^a c_B^b} + RT \ln \frac{c'_G{}^g c'_H{}^h}{c'_A{}^a c'_B{}^b} = -RT \ln K_c + RT \ln Q_c \quad [32]$$

where the concentrations  $c_A$ ,  $c_B$ ,  $c_G$ , and  $c_H$  are for equilibrium at constant pressure and the concentrations  $c'_A$ , etc., are arbitrary. If the primed values are all unity we have again the important equation for the standard free energy change,

$$\Delta F^0 = -RT \ln K_c \quad [33]$$

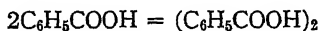
In such calculations concentrations are customarily expressed in molalities; the standard state of each solute is taken as the concentration 1 mole per 1000 g. of solvent. Molarities expressed in moles per liter also may be used if they are used throughout. The total pressure is fixed, but usually for solutions its value is not important.

To derive these expressions for dilute ideal solutions, an equilibrium box may be imagined containing a vapor phase and a large quantity of solution in which  $A$ ,  $B$ ,  $G$ , and  $H$  are in equilibrium with each other at concentrations  $c_A$ ,  $c_B$ ,  $c_G$ , and  $c_H$ . The partial pressures of the solutes are given by Henry's law, and are  $k_A c_A$ ,  $k_B c_B$ , etc. Enough inert gas is present in the vapor phase to bring the total pressure to some fixed value, say 1 atm. An isothermal, reversible process is imagined in which  $a$  moles of  $A$  are evaporated from a large amount of solution in which the concentration of  $A$  is  $c'_A$  and over which the vapor pressure of  $A$  is proportional to  $c'_A$ , i.e.,  $p_A = k_A c'_A$  by Henry's law; the vapor is compressed from the pressure  $k_A c'_A$  to  $k_A c_A$ ; and then it is introduced into the equilibrium box through a membrane permeable only to  $A$ . At the same time  $b$  moles of  $B$  are transferred to the equilibrium box, and  $g$  moles of  $G$  and  $h$  moles of  $H$  are transferred from the box in like manner. Assuming that the gas is perfect the free energy change for  $A$  is seen to be

$$\Delta F_1 = a RT \ln \frac{k_A c_A}{k_A c'_A} = a RT \ln \frac{c_A}{c'_A} \quad [34]$$

Combination with similar expressions for the other solutes gives equation (32). If the solute is relatively involatile, it is perhaps better to imagine an osmotic process of transfer; the result will be the same.

*Example 14.* The equilibrium constant for the association of benzoic acid to a dimer in dilute benzene solutions at 43.9° is  $2.7 \times 10^2$  in terms of molar concentrations. Calculate  $\Delta F^0$  and state its meaning.



$$K_c = \frac{c_{\text{dimer}}}{c_{\text{monomer}}^2} = 2.7 \times 10^2$$

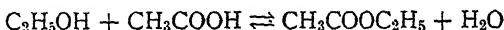
$$\begin{aligned} \Delta F^0 &= -RT \ln K_c = -1.987 \times 317.0 \times 2.303 \times 2.4314 \\ &= -3527 \text{ cal.} \end{aligned}$$

Hence there is a free energy decrease of 3527 cal. when 2 moles of benzoic acid monomer,  $\text{C}_6\text{H}_5\text{COOH}$ , at a concentration of 1 mole per liter of solution, are converted to 1 mole of benzoic acid dimer at a concentration of 1 mole per liter, in benzene at 43.9°. The reaction is spontaneous as written.

In concentrated ideal solutions the partial pressures of the solutes will be directly proportional to the mole fractions  $N_A$ , etc., rather than to the concentrations in moles per 1000 g. of solvent. Only in dilute solutions are the concentrations proportional to the mole fractions. For such solutions the expression for the free energy change is

$$\begin{aligned}\Delta F &= -RT \ln \frac{N_G^g N_H^h}{N_A^a N_B^b} + RT \ln \frac{N'_G{}^g N'_H{}^h}{N'_A{}^a N'_B{}^b} \\ &= -RT \ln K_N + RT \ln Q_N\end{aligned}\quad [35]$$

*Example 15.* Calculate  $K_N$ , assuming ideal solutions, for the following reaction at  $10^\circ$ :



if the addition of 1 mole of alcohol to 1 mole of glacial acetic acid yields at equilibrium 0.652 moles of ester. Calculate and interpret  $\Delta F^0$ .

In this equilibrium mixture

$$N_{\text{alcohol}} = N_{\text{acid}} = \frac{1.000 - 0.652}{2.000}$$

$$N_{\text{ester}} = N_{\text{water}} = \frac{0.652}{2.000}$$

$$K_N = \frac{(0.652/2.000)^2}{(0.348/2.000)^2} = \frac{(0.652)^2}{(0.348)^2} = 3.51$$

$$\begin{aligned}\Delta F^0 &= -RT \ln K_N = -1.987 \times 283.1 \times 2.303 \times \log' 3.51 \\ &= -706 \text{ cal.}\end{aligned}$$

This means that the formation of 1 mole of pure ethyl acetate and 1 mole of pure water from 1 mole of pure acetic acid and 1 mole of pure ethyl alcohol at  $10^\circ$  is attended by a free energy decrease of 706 cal.

**Activities and Fugacities.** Formulas (30) and (32) hold strictly only for perfect gases and dilute ideal solutions but the equilibrium constant and its relation to free energy change are so valuable that the above formulas are used even when the gases and solutions are not ideal. It is recognized that they are only approximately correct but they are often sufficiently exact for practical purposes.

To make possible exact calculations, G. N. Lewis introduced the terms *fugacity* and *activity*, which are defined in such a way that the equilibrium constant is a true constant and is independent of the concentrations. Fugacity has the dimensions of pressure.

Instead of writing that  $-\Delta F^0$  is approximately equal to

$RT \ln \frac{p_G^g \times p_H^h}{p_A^a \times p_B^b}$ , and that the ratio  $\frac{p_G^g \times p_H^h}{p_A^a \times p_B^b}$  is nearly constant,

one can state that equation (36), in which fugacities  $f$  are used, is exactly true at all pressures.

$$-\Delta F^0 = RT \ln \frac{f_G^g \times f_H^h}{f_A^a \times f_B^b} \quad [36]$$

Activities have the dimensions of concentrations and are in fact "effective" concentrations. If the particles of a solute exert a mutual attraction on each other, or if they combine with the solvent, or if the solvent is changed in any way so as to change the behavior of the solute, the concentrations will no longer give the same value of  $K$  over a wide range. In other words, the mass law will not apply when ordinary, analytically determined concentrations are used. In this case the activity  $a$  is defined in such a way that the mass law must hold, and equation (37) then is exact.

$$-\Delta F^0 = RT \ln \frac{a_G^g \times a_H^h}{a_A^a \times a_B^b} \quad [37]$$

The activities may be determined, as will be explained in Chapter XVIII, by referring to some standard state, i.e., to the condition of infinite dilution or to some other condition arbitrarily chosen.

It may be suggested that nothing is gained by the introduction of these arbitrary quantities; that the ability thus acquired to express laboratory facts with simple formulas is artificial. However, a great gain is made in a practical way. The relation between activities and concentration may be determined empirically for a given substance by independent experimental measurements and then many of the useful formulas of thermodynamics may be applied with exactness.

In summarizing, it may be said that the original statement of the mass law using "active masses" is correct but that the mass law does not hold strictly with ordinary substances when concentrations or pressures are used. In order to use the mass law with precision, corrected terms, called activities and fugacities, have been invented, and they must be determined by experiment. Activities may be visualized as *effective* concentrations involving the behavior of both solute and solvent. It is sometimes stated that the mass law is exact but that the "law of concentration effect" is only approximate.

In the present chapter pressures and concentrations are used, with the understanding that the results are not exact. If the pressure is not much greater than 1 atm., nor the concentration greater than

1 molal, for nonelectrolytes, the mass law may be assumed to hold within a few per cent. For electrolytes, marked deviations are found even at concentrations much lower than 1 molal, so that the introduction of activities is particularly important.

It is essential to have a clear understanding of the influence of concentration in changing the value and even the sign of  $\Delta F$ .

*Example 16.* In a simple hypothetical reaction such as a change into an isomer



if the system is at equilibrium when  $A$  and  $B$  are at equal activities,  $a_A = a_B$ , what is the value of  $\Delta F^0$ ?

$$K = \frac{a_B}{a_A} = 1 \quad \text{and} \quad \Delta F^0 = -RT \ln K = -RT \ln 1 = 0$$

*Example 17.* In another system  $C \rightleftharpoons D$  there is a state of equilibrium at  $27^\circ$  when the activity or effective concentration of the product  $D$  is ten times as great as  $C$ . What is the value of  $\Delta F^0$ ?

$$K = \frac{a_D}{a_C} = \frac{10}{1}, \quad \text{and} \quad \Delta F^0 = -RT \ln K = -2 \times 300.1 \times 2.303 \log 10 \\ = -1373 \text{ cal.}$$

If  $\Delta F^0$  has a negative sign, i.e., if the free energy of the products is less than the free energy of the reactants, there is a tendency for the reactants (the materials at the left of the reaction as written) at unit activity to react to give the products at unit activity.

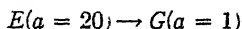
If a system is in a state of equilibrium when the activities of the products are less than those of the reactants,  $\Delta F^0$  is positive; there is no tendency for the reactants at unit activity to react to give the products at unit activity, but on the contrary the reaction tends to go in the reverse direction.

*Example 18.* In the reaction  $E \rightleftharpoons G$  there is equilibrium when the activity of the product is one-tenth that of activity of the reactant  $G$ . Calculate  $\Delta F^0$ .

$$K = \frac{a_G}{a_E} = \frac{1}{10}, \quad \Delta F^0 = -RT \ln K = -2 \times 300.1 \times 2.303 \log \frac{1}{10} \\ = -2 \times 300.1 \times 2.303 \times (-1) = +1373$$

It is clear from the positive value of  $\Delta F^0$  that  $E$  at unit activity will not react spontaneously to give  $G$  at unit activity. However some of  $E$  can be converted into  $G$  by increasing sufficiently the concentration of  $E$  or by reducing the concentration of  $G$  by removing it as it is formed.

*Example 19.* Referring to Example 18, calculate  $\Delta F$  for the reaction in which  $E$  at an activity of 20 goes to  $G$  at an activity of 1.



$$\begin{aligned}\Delta F &= -RT \ln K + RT \ln \frac{a'_G}{a'_E} = \Delta F^0 + RT \ln \frac{1}{20} \\ &= 1373 + 2 \times 300.1 \times 2.303 \times (-1.301) \\ &= 1373 - 1786 = -413\end{aligned}$$

The negative sign of  $\Delta F$  in this equation shows that the reaction will take place spontaneously under these conditions. By sufficiently increasing the concentration,  $E$  can be partially converted into  $G$  in spite of the unfavorable equilibrium constant and positive value of  $\Delta F^0$ . The distinction between  $\Delta F$  for any concentrations, and  $\Delta F^0$  for standard states at unit activity (approximately unit concentration or pressure) must be kept clearly in mind.

**Influence of Temperature on Chemical Equilibrium.** According to equation (31)

$$-\Delta F^0 = RT \ln K_p$$

Differentiating with respect to temperature

$$\frac{-d \Delta F^0}{dT} = R \ln K_p + RT \frac{d \ln K_p}{dT} \quad [38]$$

According to the Gibbs-Helmholtz equation (page 143)

$$\Delta F^0 - \Delta H^0 = T \frac{d \Delta F^0}{dT}^* \quad [39]$$

Substituting in (39) the value of  $d \Delta F^0/dT$  obtained in (38)

$$\Delta H^0 - \Delta F^0 = RT \ln K_p + RT^2 \frac{d \ln K_p}{dT} \quad [40]$$

Subtracting equation (31) from equation (40) and rearranging,

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^0}{RT^2} \quad [41]$$

This is a very important equation which is used for calculating heats of reaction from chemical equilibria, and for calculating equilibrium

\* The superscript <sup>0</sup> for both  $\Delta H$  and  $\Delta F$  indicates that the changes in heat content and free energy refer to the special case in which the reactants in their standard states (1 atm. for a gas, or 1 mole per liter and 1 atm. pressure on the solution in the case of a solute, for example) go to products in their standard states. Since the pressures are constant for  $\Delta F^0$ , partial differentiation holding  $p$  constant has been replaced by ordinary differentiation.

constants at different temperatures. The Clausius-Clapeyron equation, discussed on page 157, is a special case of this more general equation. In fact, the equilibrium constant  $K_p$  can be extended to include

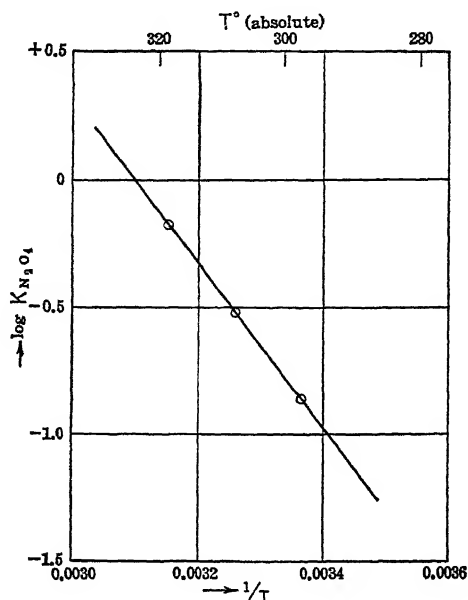


FIG. 82

any type of equilibrium such as reactions of gases, or solutes, vaporization of liquids, and sublimation or solubility of solids.

For equilibria in solutions (at constant pressure) equation (41) is written

$$\frac{d \ln K_c}{dT} = \frac{\Delta H^0}{RT^2} \quad [42]$$

For gaseous equilibria, where  $K_p = K_c(RT)^{\Delta n}$  it can be proved that

$$\frac{d \ln K_c}{dT} = \frac{\Delta E^0}{RT^2} \quad [43]$$

Over small temperature ranges  $\Delta H$  can be assumed to be constant, and integration of equation (41) gives

$$\ln K_p = -\frac{\Delta H^0}{R} \frac{1}{T} + C \quad [44]$$

Data are given in the following table for the dissociation of nitrogen tetroxide. In Fig. 82 values of  $\log K_p$  for the dissociation of nitrogen

tetroxide are plotted against  $1/T$ , and it is evident that a straight line is produced. Such a result is to be expected from equation (44), and, in fact, the heat of dissociation,  $\Delta H^\circ$ , can be calculated from the slope of the line, as follows:

$$\Delta H^\circ = -\text{slope} \times 2.303R \quad [45]$$

For nitrogen tetroxide  $\Delta H^\circ$  is 14,600, since the slope is  $-3188.7$  and  $R$  is 1.987 cal.

TABLE V  
DISSOCIATION CONSTANTS OF  $N_2O_4$

$T$	$K$	$1/T$	$\log K$
288.1°	0.060	0.003472	-1.222
298.1	0.141	0.003356	-0.850
308.1	0.315	0.003247	-0.502
318.1	0.664	0.003145	-0.178
328.1	1.349	0.003048	+0.130
338.1	2.607	0.002958	+0.416
348.1	4.867	0.002873	+0.687

The value of the integration constant  $C$  in equation (44) can be determined from experimental values of  $K_p$  at definite temperatures, and the practical working equation becomes

$$\log K_p = \frac{-14,600}{2.303 \times 1.987T} + 9.8500$$

It is evident that  $K_p$  becomes larger as the temperature increases, i.e., the dissociation becomes greater. Also, according to equation (31) the decrease in free energy becomes greater, indicating greater dissociation. Equation (41) can be solved also by integrating between limits  $K_{p_2}$  at  $T_2$  and  $K_{p_1}$  at the lower temperature  $T_1$ , as was done on page 158.

$$\begin{aligned} \ln K_{p_2} - \ln K_{p_1} &= \frac{-\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\ \log \frac{K_{p_2}}{K_{p_1}} &= \frac{\Delta H^\circ}{2.303R} \left( \frac{T_2 - T_1}{T_2 \times T_1} \right) \end{aligned} \quad [46]$$

*Example 20.* Calculate the heat of dissociation of nitrogen tetroxide from the data at 298.1 and 338.1 given in Table V.

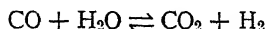
$$\log \frac{K_{p_2}}{K_{p_1}} = \log \frac{2.607}{0.141} = \frac{\Delta H^\circ}{2.303 \times 1.987} \left( \frac{338.1 - 298.1}{338.1 \times 298.1} \right)$$

and

$$\Delta H^\circ = 14,610$$



*Example 21.* The equilibrium constant  $K_p$  for the reaction



is 10 at  $690^\circ \text{K}$ . The heat of the reaction,  $\Delta H^\circ$ , is  $-10,200 \text{ cal}$ . Calculate the partial pressure of each of the gases in an equilibrium mixture prepared by mixing 0.400 mole of CO and 0.200 mole of  $\text{H}_2\text{O}$  in a volume of 5 liters at  $500^\circ \text{K}$ .

$$\log \frac{K_{690^\circ \text{K.}}}{K_{500^\circ \text{K.}}} = \frac{-10,200(690 - 500)}{2.303 \times 1.987 \times 500 \times 690} = -1.2275$$

$$\log K_{500^\circ \text{K.}} = \log 10 + 1.2275 = 2.2275 \quad K_{500^\circ \text{K.}} = 169$$

Let  $x$  = number of moles of  $\text{CO}_2$ , and  $\text{H}_2$  produced.

$$K_p = 169 = \frac{\left(x \frac{RT}{v}\right) \left(x \frac{RT}{v}\right)}{\left[(0.4 - x) \frac{RT}{v}\right] \left[(0.2 - x) \frac{RT}{v}\right]} = \frac{x^2}{(0.4 - x)(0.2 - x)}$$

$$x = 0.199$$

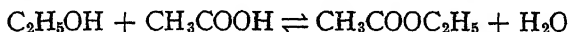
$$p_{\text{CO}_2} = p_{\text{H}_2} = \frac{n RT}{v} = \frac{0.199 \times 0.08205 \times 500.0}{5} = 1.63 \text{ atm.}$$

$$p_{\text{CO}} = \frac{(0.4 - 0.199) \times 0.08205 \times 500.0}{5} = 1.65 \text{ atm.}$$

$$p_{\text{H}_2\text{O}} = \frac{(0.2 - 0.199) \times 0.08205 \times 500.0}{5} = 0.01 \text{ atm.}$$

If the heat of reaction at constant pressure is zero, the right-hand sides of equations (41) or (42) become equal to zero. In other words, in such a reaction a change in temperature does not cause a displacement of the equilibrium.

The reaction



is accompanied by such a small thermal change that it may be considered as zero. According to the above reasoning, there should be only a very slight displacement of the equilibrium when the temperature is varied. Berthelot found that, at  $10^\circ$ , 65.2 per cent of the alcohol and acid are changed into ester, and at  $220^\circ$ , 66.5 per cent of the mixture is transformed into ester. Thus, an increase of  $210^\circ$  produces hardly any displacement of the equilibrium.

**Equilibria Involving Solids and Gases.** The calculation of an equilibrium constant is simplified if one or more of the substances taking part in the equilibrium is a solid or a liquid. As long as the

solid or liquid is present the partial pressure of the gas remains fixed and equal to the vapor pressure. Moreover, this pressure is independent of the amount of solid or liquid present. This constant pressure can then be incorporated in the equilibrium constant. Pure solids and liquids and the vapors in equilibrium with them are usually assigned activities of unity, and so they can be neglected in writing the expression for the equilibrium constant. Thus for the reaction



the equilibrium constant may be written

$$K'_p = \frac{p_{\text{CaO}} \times p_{\text{CO}_2}}{p_{\text{CaCO}_3}}$$

Since  $p_{\text{CaO}}$  and  $p_{\text{CaCO}_3}$  are constant at any one temperature, they do not really affect the equilibrium and the constant  $K_p$  is used where

$$K_p = p_{\text{CO}_2} \quad [47]$$

The relation between  $K_p$  and  $K'_p$  is

$$K_p = K'_p \frac{p_{\text{CaCO}_3}}{p_{\text{CaO}}}$$

The equilibrium constant, at any one temperature, is determined solely by the pressure of the carbon dioxide evolved. Table VI gives the values of the pressure of carbon dioxide corresponding to various temperatures.

TABLE VI  
DISSOCIATION PRESSURES OF  $\text{CaCO}_3$

Temperature, Degrees C.	Pressure in Atmospheres
500	0.000096
600	0.00242
700	0.0292
800	0.220
897	1.000
1000	3.871
1100	11.499
1200	28.680

When solid ammonium hydrosulfide is heated, it is almost completely dissociated into ammonia and hydrogen sulfide, as shown by the following equation:



This reaction was investigated by Isambert, who found that the total gas pressure at 25.1° is equal to 0.66 atm. Since the partial pressures of the ammonia and hydrogen sulfide are necessarily the same, each must be approximately equal to 0.33 atm., the relatively small pressure due to the undissociated vapor of the ammonium hydrosulfide being neglected. Writing an equilibrium constant for this reaction and remembering that  $p_{\text{NH}_4\text{HS}}$ , the vapor pressure of the solid ammonium hydrosulfide, is constant,

$$K'_p = \frac{p_{\text{NH}_3} \times p_{\text{H}_2\text{S}}}{p_{\text{NH}_4\text{HS}}}. \quad K_p = p_{\text{NH}_3} \times p_{\text{H}_2\text{S}} \quad [48]$$

where  $K_p$  is a constant at a given temperature.

According to Dalton's law of partial pressures

$$P = p_{\text{NH}_3} + p_{\text{H}_2\text{S}} + p_{\text{NH}_4\text{HS}}$$

where  $P$  is the total pressure. Neglecting the relatively small pressure  $p_{\text{NH}_4\text{HS}}$

$$P = p_{\text{NH}_3} + p_{\text{H}_2\text{S}}$$

It must be clearly understood that  $p_{\text{NH}_4\text{HS}}$  is neglected in determining the total pressure because it is small, but that it disappears in the equilibrium constant  $K$  not because it is small but because it is *constant*. Hence, since  $p_{\text{NH}_3} = p_{\text{H}_2\text{S}}$

$$\frac{P}{2} = p_{\text{NH}_3} = p_{\text{H}_2\text{S}}$$

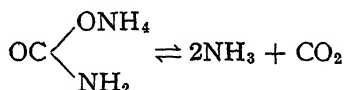
Substituting these values in equation (48)

$$K_p = \frac{P^2}{4} = \frac{(0.66)^2}{4} = 0.109$$

The value of the equilibrium constant may be checked by observing the effect on the system of the addition of an excess of either one of the products of the dissociation. Table VII gives the results of a few of Isambert's experiments.

As will be seen, the mean value of the equilibrium constant agrees well with the value found for equivalent amounts of the products of dissociation.

The dissociation of ammonium carbamate takes place according to the equation



This dissociation has been very carefully investigated by Briggs and Migrdichian.\*

\* Briggs and Migrdichian, *J. Phys. Chem.*, **28**, 1121 (1924).

Applying the law of mass action and remembering that the solid ammonium carbamate does not affect the equilibrium

$$K_p = p_{\text{NH}_3}^2 \times p_{\text{CO}_2} \quad [49]$$

The total pressure  $P$  is due to 3 moles of gas ( $2\text{NH}_3 + \text{CO}_2$ ), since the small vapor pressure of the solid may be neglected at room temperature. Then

$$p_{\text{NH}_3} = \frac{2}{3}P \quad \text{and} \quad p_{\text{CO}_2} = \frac{1}{3}P$$

and substituting in equation (49)

$$K_p = \frac{4P^3}{27} \quad [50]$$

At a definite temperature  $K_p$  has a fairly constant value even when an excess of ammonia or carbon dioxide is added.

TABLE VII  
EQUILIBRIUM PRESSURES OF  $\text{NH}_4\text{HS}$  ( $25.1^\circ$ )

Pressure of Ammonia	Pressure of Hydrogen Sulfide	$p_{\text{NH}_3} \times p_{\text{H}_2\text{S}} = K_p$
0.274	0.387	0.106
0.182	0.603	0.110
0.549	0.192	0.105
0.596	0.188	0.112
		Mean 0.108

*Example 22.* For the reaction  $\text{C} (s) + 2\text{H}_2 \rightleftharpoons \text{CH}_4$  at  $1000^\circ$ ,  $K_p = 0.263$ . Calculate the total pressure at equilibrium when 0.100 mole of  $\text{CH}_4$  is placed in a volume of 2 liters at  $1000^\circ$ . Let  $x$  = the number of moles of  $\text{CH}_4$  which dissociate.

$$p_{\text{CH}_4} = \frac{nRT}{v} = \frac{(0.1 - x)(0.08205)(1273)}{2} = 5.22 - 52.2x$$

$$p_{\text{H}_2} = \frac{nRT}{v} = \frac{2x(0.08205)(1273)}{2} = 104x$$

$$K_p = 0.263 = \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2} = \frac{5.22 - 52.2x}{(104x)^2} \cdot x = 0.035$$

$$p_{\text{CH}_4} = \frac{(0.1 - 0.035)(0.08205)(1273)}{2} = 3.4$$

$$p_{\text{H}_2} = \frac{2(0.035)(0.08205)(1273)}{2} = 3.7$$

$$\text{Total pressure} = 3.4 + 3.7 = 7.1 \text{ atm.}$$

**Distribution of a Solute between Two Immiscible Solvents.** A volatile solute may escape from its solution into a surrounding gas space, or it may escape into another immiscible liquid with which the solution is in contact. An equilibrium is set up and the calculation of an equilibrium constant may be made. This special kind of an equilibrium constant is called a distribution coefficient. When an aqueous solution of succinic acid is shaken with ether, the acid distributes itself between the ether and the water in such a way that the ratio between the two concentrations is always constant. Nernst showed that, if the molecular weight of the solute is the same in both solvents, the ratio in which it distributes itself between them is constant at constant temperature. If there are several solutes in solution, the distribution of each solute is the same as if it were present alone. This is analogous to Dalton's law of partial pressures. Table VIII gives the results of three experiments on the distribution of succinic acid between ether and water.

TABLE VIII  
DISTRIBUTION OF SUCCINIC ACID (14°)

Concentration in Water	Concentration in Ether	Distribution Coefficient
43.4	7.1	6.1
43.8	7.4	5.9
47.4	7.9	6.0

As will be seen, the distribution coefficient is constant, showing that Henry's law applies.

When the molecular weight of a solute is different in the two solvents, the distribution coefficient is not constant and conversely, if the distribution coefficient is not constant it may be inferred that the molecular weights of the solute in the two solvents are not identical.

If, for example, a substance is associated into a double molecule in one solvent but has a normal molecular weight (equal to the sum of the atomic weights) in the other, the equilibrium may be written  $A_2 \rightleftharpoons 2A$  and the equilibrium constant is given by the formula

$$K_c = \frac{c_A^2}{c_{A_2}} \quad [51]$$

In the more general case where the molecule associates into  $n$  molecules  $A_n \rightleftharpoons nA$ , and

$$K_c = \frac{c_A^n}{c_{A_n}} \quad [52]$$

The distribution of benzoic acid between benzene and water is shown in Table IX, where concentrations are expressed in moles per liter,  $c_w$  in water, and  $c_b$  in benzene.

The values of the ratio  $c_w/c_b$  steadily decrease with increasing concentration of the acid, while, on the other hand, the values of the ratio  $c_w^2/c_b$  remain relatively constant. This fact shows that benzoic acid has twice the normal molecular weight in benzene.

This fact is fully corroborated by direct measurements of molecular weight, the elevation of the boiling point in benzene being roughly half as large as would be expected on the assumption that the molecular weight is the sum of the atomic weights in the formula  $C_6H_5COOH$ .

TABLE IX  
DISTRIBUTION OF BENZOIC ACID (20°)

$c_w$ (Water)	$c_b$ (Benzene)	$\frac{c_w}{c_b}$	$\frac{c_w^2}{c_b}$
0.0150	0.242	0.062	0.00093
0.0195	0.412	0.048	0.00092
0.0289	0.970	0.030	0.00036

When the solute is very sparingly soluble, the distribution ratio is identical with the ratio of solubilities if the two molecular weights are the same. The small numerical value of the distribution ratio in Table IX indicates that benzoic acid is less soluble in water than in benzene. In most cases, however, the saturated solutions are so concentrated and so far from ideal that the mass law no longer holds. Under these conditions the coefficient of distribution changes somewhat with the concentration, and the distribution ratio in dilute solution may differ largely from the solubility ratio. The distribution ratio can be made constant at all concentrations by using activities in place of concentrations (pages 292 and 521).

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## PROBLEMS

1. At  $630^\circ$  and 1 atm. the density of the gas obtained by vaporizing  $\text{SO}_3$  is 0.000927 g. per ml. Calculate: (a) the degree of dissociation of  $\text{SO}_3$  into  $\text{SO}_2$  and  $\text{O}_2$ ; (b) the equilibrium constant of the reaction. *Ans.* (a) 0.331. (b) 0.0347.

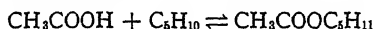
2. For the gaseous reaction  $\text{COCl}_2 \rightleftharpoons \text{CO} + \text{Cl}_2$  at  $100^\circ$ , the dissociation constant  $K_p$  is  $6.7 \times 10^{-9}$ . Calculate the partial pressure of carbon monoxide in equilibrium with phosgene at this temperature under a total pressure of 2 atm. The dissociation is so slight that the partial pressure of phosgene may be taken as equal to the total pressure. *Ans.*  $1.16 \times 10^{-4}$ .

3. At  $1000^\circ$  for the reaction  $\text{I}_2 \rightleftharpoons 2\text{I}$ ,  $K_c = 0.165$ . If one mole of iodine is placed in a 100-ml. flask and heated to  $1000^\circ$ , how much is left undecomposed? *Ans.* 0.938.

4.  $\Delta H$  for the gaseous reaction  $\text{C}_2\text{H}_2 + \text{D}_2\text{O} \rightleftharpoons \text{C}_2\text{D}_2 + \text{H}_2\text{O}$  is 530 cal. At  $25^\circ$   $K_p$  is 0.82. How much  $\text{C}_2\text{D}_2$  is formed if a mole of  $\text{C}_2\text{H}_2$  and 2 moles of  $\text{D}_2\text{O}$  are put together at a total pressure of 1 atm. and at  $100^\circ$ ? Assume that the reactants and products have equal heat capacities and behave as perfect gases. *Ans.* 0.66.

5. For the reaction  $A + B \rightarrow AB$ ,  $\Delta F^\circ = -2000$  cal. at  $27^\circ$ . Under what total pressure must an equimolecular gaseous mixture be placed in order to produce a 40 per cent conversion into  $AB$ ? *Ans.* 0.062 atm.

6. When 0.00645 mole of amylene and 0.001 mole of acetic acid are mixed in 845 ml. of an inert solvent, 0.000784 mole of ester is formed according to the reaction



How much ester will be formed when one mixes 0.00584 mole of amylene and 0.001 mole of acetic acid in 575 ml.? *Ans.* 0.000487.

7. Mercuric oxide dissociates according to the reaction,  $2\text{HgO} = 2\text{Hg}(g) + \text{O}_2$ . At  $420^\circ$  the dissociation pressure is 387 mm., and at  $450^\circ$  it is 810 mm. Calculate (a) the dissociation constants, and (b) the heat of dissociation per mole. *Ans.* (a) 0.0196; 0.1794 atm. (b) 36,750 cal. per mole.

8. At  $1273^\circ$  K. and at a total pressure of 30 atm. the equilibrium in the reaction  $\text{CO}_2 + \text{C}(s) \rightleftharpoons 2\text{CO}$  is such that 17 molar per cent of the gas is  $\text{CO}_2$ . (a) What percentage would be  $\text{CO}_2$  if the total pressure were 20 atm.? (b) What would be the effect on the equilibrium of adding  $\text{N}_2$  until the partial pressure of  $\text{N}_2$  is 10 atm.? (c) At what pressure will 25 per cent of the gas be  $\text{CO}_2$ ? *Ans.* (a) 12.5%. (b) No effect. (c) 54 atm.

9. The distribution coefficient at  $25^\circ$  of lactic acid between water and chloroform  $c_{\text{CHCl}_3}/c_{\text{H}_2\text{O}}$  expressed in moles per liter is 0.0203. How much lactic acid will be extracted from 100 ml. of a 0.8 molar solution of lactic acid in chloroform by shaking with 100 ml. of water? *Ans.* 0.0784 mole.

10. Calculate the value of  $x$  in Table II.

11. (a) At what total pressure will  $\text{PCl}_5$  be dissociated at  $250^\circ$  to the extent of 20 per cent into  $\text{PCl}_3$  and  $\text{Cl}_2$ ?  $K_p = 1.78$ .

(b) What is the weight of a liter of the partially dissociated gas at this temperature and pressure?

12. The following equation has been found to apply to the reaction  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$

$$\log K_p = -\frac{14,600}{4.576T} + 9.850$$

(a) Calculate the value of  $K_p$  at  $50^\circ$ .

(b) Calculate the degree of dissociation at this temperature when the total pressure is 1 atmosphere.

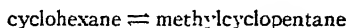
13. For the reaction  $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$  at  $698.6^\circ \text{K}$ ,  $K_p = 1.83$ . How many grams of hydriodic acid will be formed when 10 g. iodine and 0.1 g. of hydrogen are heated to this temperature in a 2-liter vessel. What will be the partial pressures of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$ ?

14. For the reaction  $\frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2 = \text{NO}$ ,  $K_p = 0.0332$  at  $2200^\circ \text{K}$ .

(a) What per cent by volume of nitric oxide is in equilibrium with air (21 per cent oxygen and 79 per cent nitrogen) at this temperature?

(b) After a certain explosion the gases contain 5 per cent oxygen and 50 per cent nitrogen together with nitric oxide, carbon dioxide and other gases. Calculate the molar per cent of the gas mixture which exists as nitric oxide at  $2200^\circ \text{K}$ .

15. The following reaction takes place in the presence of aluminum chloride:

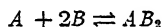


From the following data, calculate: (a)  $\Delta F^\circ$  at  $25^\circ$ . (b)  $\Delta H$  at  $25^\circ$ .

Temperature	$K_c$
$25^\circ$	0.143
45	0.193
65	0.272

16. What is the free energy change when 1 mole of  $\text{N}_2\text{O}_4$  at  $25^\circ$  and 2 atm. is converted into 2 moles of  $\text{NO}_2$  at 0.1 atm? For the reaction  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  at  $25^\circ$   $K_p = 0.141$ .

17. For the gaseous reaction at  $200^\circ$



$\Delta F^\circ = 1000$  cal. When 2 moles of  $B$  is mixed with one mole of  $A$ , what total pressure must be applied in order to produce a 70 per cent conversion of  $A$  into  $AB_2$ ?

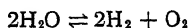
18. The equilibrium pressure of solid  $\text{NH}_4\text{HS}$  is 500 mm. at  $25^\circ$ . Assuming that the vapor is completely decomposed into  $\text{NH}_3$  and  $\text{H}_2\text{S}$ , calculate the maximum pressure of  $\text{H}_2\text{S}$  which can be added to a system containing  $\text{NH}_3$  at 50 mm. without precipitating  $\text{NH}_4\text{HS}$ .

19. The heat of solution of acetic acid in water is  $-4180$  cal. and in chloroform  $-8778$  cal. At  $20^\circ$  the distribution coefficient  $K = c_w/c_{\text{CHCl}_3} = 14.05$ . What is the distribution coefficient at  $30^\circ$ ?

20. The data for the solubility of urea in water are given below. Calculate the heat of solution of urea in  $\text{H}_2\text{O}$ . Up to what concentration may this solution be considered ideal? For ideal solutions the differential heat of solution is equivalent to the heat of fusion of the substance.

$N_{\text{urea}}$	1.000	0.9004	0.8190	0.7217	0.5680	0.4741
$t^\circ$	132.6	123.2	115.3	104.4	84.4	68.5

21. When water is heated to  $1700^\circ$  at 1 atmosphere, 99.9 molar per cent remains as  $\text{H}_2\text{O}$  and 0.1 molar per cent dissociates according to the reaction





Calculate  $K_p$  and the corresponding value of  $\Delta F^0$  at this temperature. Calculate  $K_c$ .

22. When sulfur dioxide is oxidized to sulfur trioxide in the presence of a catalyst at 727° the following relation holds:

$$K_p = 1.85 = \left( \frac{p_{\text{SO}_3}}{p_{\text{SO}_2}} \right) \times \frac{1}{\sqrt{p_{\text{O}_2}}}$$

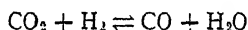
(a) What is the ratio of  $\text{SO}_3$  to  $\text{SO}_2$  when the partial pressure of oxygen at equilibrium is 0.3 atm.?

(b) What is the ratio of  $\text{SO}_3$  to  $\text{SO}_2$  when the partial pressure of oxygen is 0.6 atm. at equilibrium?

(c) What is the effect on the ratio  $\text{SO}_3/\text{SO}_2$  when an equilibrium mixture containing 0.3 atm. of oxygen is compressed so that the total pressure is doubled?

(d) What is the effect on the ratio  $\text{SO}_3/\text{SO}_2$  if the total pressure of the mixture of gases is increased by forcing in nitrogen under pressure?

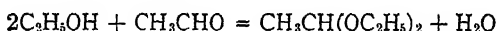
23. When 1 mole of  $\text{CO}_2$  and 1 mole of  $\text{H}_2$  were heated in a liter vessel to 1005°, it was found that 0.56 mole of  $\text{H}_2\text{O}$  was formed. Calculate  $\Delta F^0$  at 1005° for the reaction



24. Calculate the total pressure which must be applied to a mixture of three parts of hydrogen and one part of nitrogen to give a mixture containing 10 per cent ammonia at 400°. At 400°,  $K_p = 1.64 \times 10^{-4}$  for the reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ .

25. Calculate the value of  $\gamma$  in Table IV.

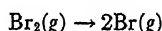
26. Adkins and Adams studied the equilibria involved in the formation of acetals by titrating the mixture and determining the aldehyde concentration. At 25°, 1 mole of ethanol was mixed with 0.091 mole of acetaldehyde in a volume of 63.0 ml., and it was found that, when equilibrium was reached, 90.72 per cent of the acetaldehyde had reacted. The reaction is:



(a) Calculate the equilibrium constant, assuming an ideal solution.

(b) If the mixture is diluted to 500 ml. with an inert solvent, what per cent of acetaldehyde will have reacted?

27. The following data apply to the reaction



$T$	1073	1123	1173	1223	1273	1323° K.
$K_p$	0.000179	0.000403	0.00140	0.00328	0.0071	0.0182

Determine by graphical means the heat change involved when one mole of  $\text{Br}_2$  dissociates completely.

28. At 56.0° the solubility of *p*-hydroxybenzoic acid is 3.31 g. per 100 g. of water; at 80.0° it is 13.43 g. per 100 g. of water. What is the solubility at 40°?

29. Ten grams of calcium carbonate is placed in a container of 1 liter capacity and heated to 800°. How many grams of calcium carbonate remain undecomposed? If the amount of  $\text{CaCO}_3$  were 20 g., how much would remain undecomposed?

30. Picric acid distributes itself between the two immiscible solvents, benzene and water, at different concentrations as follows:

<i>Conc. in Water Phase</i>	<i>Conc. in Benzene Phase</i>
0.00208 mole/liter	0.000932 moles/liter
0.00327 "	0.00225 "
0.00701 "	0.0101 "
0.0101 "	0.0199 "

Picric acid exists as non-dissociated and nonassociated  $\text{C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$  in benzene. What conclusions can you draw regarding dissociation or association in the water phase?

31. Derive an equation for  $K_p$  in terms of  $\alpha$  and  $P$  for the reaction  $2A \rightleftharpoons 2B + C$ , both reactant and products being gaseous. Show that, at very large values of  $P$  and  $K_p$ ,  $\alpha$  varies inversely as the cube root of  $P$ .

32. For the reaction  $2\text{NaHCO}_3 \rightleftharpoons \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)$ ,  $K_p = 0.23$  at  $100^\circ$ . On a day when the barometric pressure was 740 mm., the room temperature  $27^\circ$ , and the relative humidity 0.70, 20 g. of solid sodium bicarbonate was placed in a 5-liter flask and sealed with the air from the room. It was then brought up to  $100^\circ$ . (a) What was the partial pressure of  $\text{CO}_2$  at equilibrium in the flask (neglecting the carbon dioxide of the air)? The vapor pressure of water at  $27^\circ$  is 26.8 mm. (b) What was the pressure in the flask?

33. A certain optically active organic compound slowly racemized in solution, and eventually the solution showed no optical rotation, the  $d$  and  $l$  forms being in equal concentrations. When the temperature of the solution was varied over wide limits there was no return of optical activity. What facts can be deduced about  $\Delta F^\circ$  and  $\Delta H^\circ$  for the racemization reaction?

34. For the reaction  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ ,  $K_p$  at  $25^\circ$  is 0.141. What pressure would be expected if 1 g. of liquid  $\text{N}_2\text{O}_4$  is allowed to evaporate into a liter vessel at this temperature? Assume that  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are perfect gases.

35. The percentage conversion of ethyl alcohol and acetic acid to give ethyl acetate is not the same when the two liquids are mixed and when the vapors are passed over silica gel at the same temperature. This fact, however, does not violate the principle that the equilibrium is unaffected by a catalyst. Explain.

36. For the reaction  $\text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) \rightleftharpoons 2\text{Fe}(s) + 3\text{CO}_2(g)$  the following values of  $K_p$  are known:

$t^\circ\text{C}$	100	250	1000
$K_p$	1100	100	0.0721

At  $1120^\circ$  for the reaction  $2\text{CO}_2(g) \rightleftharpoons 2\text{CO}(g) + \text{O}_2(g)$ ,  $K_p = 1.4 \times 10^{-12}$ . What equilibrium partial pressure of  $\text{O}_2$  would have to be supplied to a vessel at  $1120^\circ$  containing 1 mole of solid  $\text{Fe}_2\text{O}_3$  in order just to prevent the formation of  $\text{Fe}$ ?

## CHAPTER XIII

### PHASE DIAGRAMS

**Heterogeneous Systems.** Systems which are made up of matter in different states of aggregation are termed *heterogeneous systems*, as distinguished from homogeneous systems, where the composition is uniform throughout. The physically distinct portions of matter involved in a heterogeneous system are known as *phases*, each phase being homogeneous and having uniform physical and chemical properties, and being separated from the other phases by definite bounding surfaces. Thus, ice, liquid water, and vapor are phases, and any two of these, or all three of them taken together, constitute a heterogeneous system. Another heterogeneous system is formed by calcium carbonate and its products of dissociation, calcium oxide and carbon dioxide. The equilibrium between a solid, its saturated solution, and vapor affords an illustration of a still more complex heterogeneous system.

The conditions under which these different phases can exist is a matter of considerable practical importance and the experimental determinations of these conditions are conveniently recorded in various kinds of diagrams. It is the purpose of this chapter to describe these different types of heterogeneous systems and to show how the diagrams may be interpreted and used.

The chief variables which determine the state of equilibrium are temperature, pressure, and, in systems containing more than one independent chemical substance, the concentration of the different substances in the several phases. Time is not a variable, for the considerations apply to systems which are in equilibrium. It must be clearly understood that only relative quantities are involved and not the total quantity of material. The same diagram applies whether grams or tons of material are involved.

**Temperature and Pressure in the System, Water, Ice, Vapor.** The conditions of temperature and pressure under which ice, liquid water, and vapor can exist in a state of equilibrium have been determined by experiment and are given in Fig. 83 (which is not drawn to scale on account of the large range of pressures).

Three general areas are labeled in which ice, water, or vapor can

exist alone. For example, vapor may exist anywhere in the area labeled "vapor," and it is necessary to specify both the pressure and the temperature in order to define the system completely. The mere statement that water vapor is present at a specified pressure does not describe the system, because the temperature variable is not defined.

Where two of these areas touch there is a line and along each line the two phases exist in equilibrium.

The vapor-pressure curve of water is represented by the line  $OA$ . Above this line liquid water exists alone; and below it water vapor exists alone. Only on the line  $OA$  where both regions touch is it possible to have both water and its vapor in equilibrium. Thus, if the pressure is reduced to a point below the line  $OA$ , all the water will be vaporized; if, on the other hand, the pressure is raised above the curve, all the vapor will

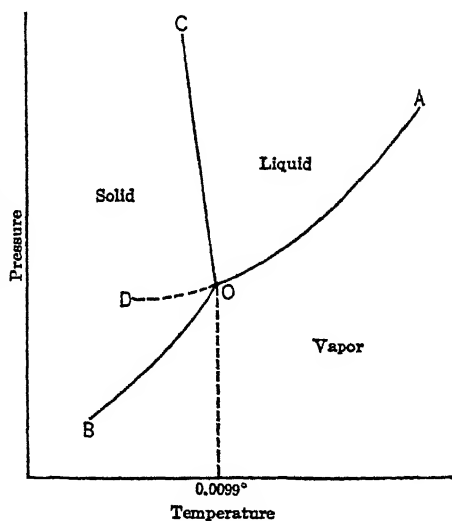


FIG. 83

ultimately condense to the liquid state. If it is stated that the system contains *both* liquid water and water vapor at  $25^{\circ}$ , it is not necessary to specify the pressure because it has been found by experiment that water and its vapor can exist together at  $25^{\circ}$  only under a pressure of 23.7 mm. The pressure at any temperature may be read from the vapor-pressure curve. Likewise if the pressure is stated the temperature may be determined from the graph. A single variable, either temperature or pressure, is sufficient to describe completely the system along a line.

The line  $BO$  is the sublimation curve of ice. Above it lies ice and below it lies vapor. Only along  $BO$  can ice and vapor exist together in equilibrium.

The line  $OC$  shows how the melting point changes with pressure. At all points on the line the pressure is greater than the vapor pressure, as given by the line  $BOA$ ; so it may be concluded that no vapor is present. This line is inclined toward the vertical axis and the melting point of ice is lowered by increasing the pressure — a fact which can be predicted from the principle of Le Chatelier, since the liquid water

occupies a smaller volume than the solid ice. Along  $OC$  there are two phases, ice and liquid water, and again it is necessary to specify only one variable, either temperature or pressure, to describe the system completely.

Where the three lines, representing pairs of phases, intersect, the three areas touch and all three phases exist together in equilibrium. Only one such point is possible with three phases and it is called a triple point. It is not necessary to specify either temperature or pressure under these conditions, for there is only one possible temperature and one possible pressure which will permit all three phases to exist together in equilibrium. If the temperature is raised at constant pressure the ice will melt and the liquid will vaporize leaving only vapor; if the temperature is lowered, there will be only ice; if the pressure on the vapor is raised at constant temperature, the vapor will condense; and, finally, if the pressure is lowered, the liquid and ice will evaporate.

Ice and water, saturated with air, are in equilibrium with their vapor in air under atmospheric pressure at a temperature of  $0^{\circ}$ . The definition of the centigrade scale depends on this fact. The situation is somewhat complicated because the pressure of water vapor is only 4.57 mm. whereas the total pressure on the ice and water is 1 atm.

If ice and water, from which dissolved air has been removed, are allowed to evaporate into a previously evacuated space, the pressure on the ice and water will be 4.57 mm. instead of 1 atm., and the melting point will be slightly higher. The exact temperature of this triple point is  $0.0099^{\circ}$ . This difference of  $0.0099^{\circ}$  is due to two different factors. The solubility of air at atmospheric pressure is sufficient to lower the freezing point by  $0.0024^{\circ}$  and the increase of pressure from 4.57 mm. to one atm. lowers the freezing point  $0.0075^{\circ}$ . This lowering of  $0.0075^{\circ}$  due to the pressure change checks with that calculated by the Clapeyron equation. The two effects together bring the freezing point from  $0.0099^{\circ}$  down to  $0^{\circ}$ .

The dotted curve  $OD$ , which is a continuation of  $OA$ , represents the vapor pressure of supercooled water. It will be noticed that there is no break in the vapor-pressure curve as long as the solid phase does not separate, and that the vapor pressure of supercooled water, which is an unstable phase, is greater than that of the stable phase, ice, at the same temperature.

The lower limit of the sublimation curve  $OB$  is theoretically determined by the absolute zero; the vaporization curve  $OA$  terminates at  $A$  which is the critical temperature,  $374^{\circ}$ , corresponding to a pressure of 217.7 atm. Above this critical temperature it is not possible to

have the liquid phase. Investigations conducted by Bridgman with a view to determining the course of the fusion curve  $OC$  have revealed the existence of seven different crystalline modifications of ice, all of which, with the exception of ordinary ice, are denser than water. The first of these new forms of ice makes its appearance at a pressure of 2115 kg. per square centimeter, and the last at a pressure of 22,400.

**Concentration, Temperature, and Pressure.** When two or more chemical individuals are involved, the concentration of these materials as well as temperature and pressure are variables which must be specified in order to define the system completely. If there are but two substances as a salt and water, concentration may be plotted along one axis and temperature and pressure along two other axes giving a space model in three dimensions. Such a model is shown in Fig. 84a for the system copper sulfate and water; temperature is plotted horizontally along the  $X$  axis. The concentration of water is plotted vertically along the  $Z$  axis, and pressure is plotted along the  $Y$  axis at right angles to the other two. The concentrations of water corresponding to the various crystalline salt hydrates and the saturated solution are given on the concentration axis. Sections may be cut by planes at right angles to the three axes giving respectively a  $C$ - $P$  diagram at constant temperature, a  $C$ - $T$  diagram at constant pressure and a  $P$ - $T$  diagram at constant concentration. In the concentration-pressure diagram, curves are given for one constant temperature at  $50^\circ$ . The concentration-temperature relations at a constant pressure of 30 mm. are shown in Fig. 84c. In the pressure-temperature diagram, shown in Fig. 84d the intersections of the space model by horizontal planes are given for concentrations corresponding to each of the salt hydrates and the saturated solution. The lines in Fig. 84d may be regarded as projections onto the basal plane. Water vapor exists in the region in front of the space model. Only condensed phases, salt hydrates and solution exist inside of it.

The  $C$ - $P$  diagram, shown in Fig. 84b, illustrates the behavior of a solution of copper sulfate when it is placed in a dessicator at  $50^\circ$  provided with a manometer and allowed to lose water gradually until only the anhydrous salt remains.

As water is removed from the solution the concentration of copper sulfate increases and the vapor pressure of the solution decreases along the line  $LM$ . When the solution becomes saturated the pressure remains constant, as shown by the vertical line at  $M$ , while the water is removed from the saturated solution. Finally when all the solution has disappeared the pressure drops abruptly to 47 mm. at  $N$ . The pressure over completely hydrated copper sulfate in a thin layer

remains constant at 47 mm., until the salt has been deprived of 2 moles of water, when it drops abruptly to 30 mm. at *O*, and remains constant until 2 more moles of water have been lost at *P*. It then

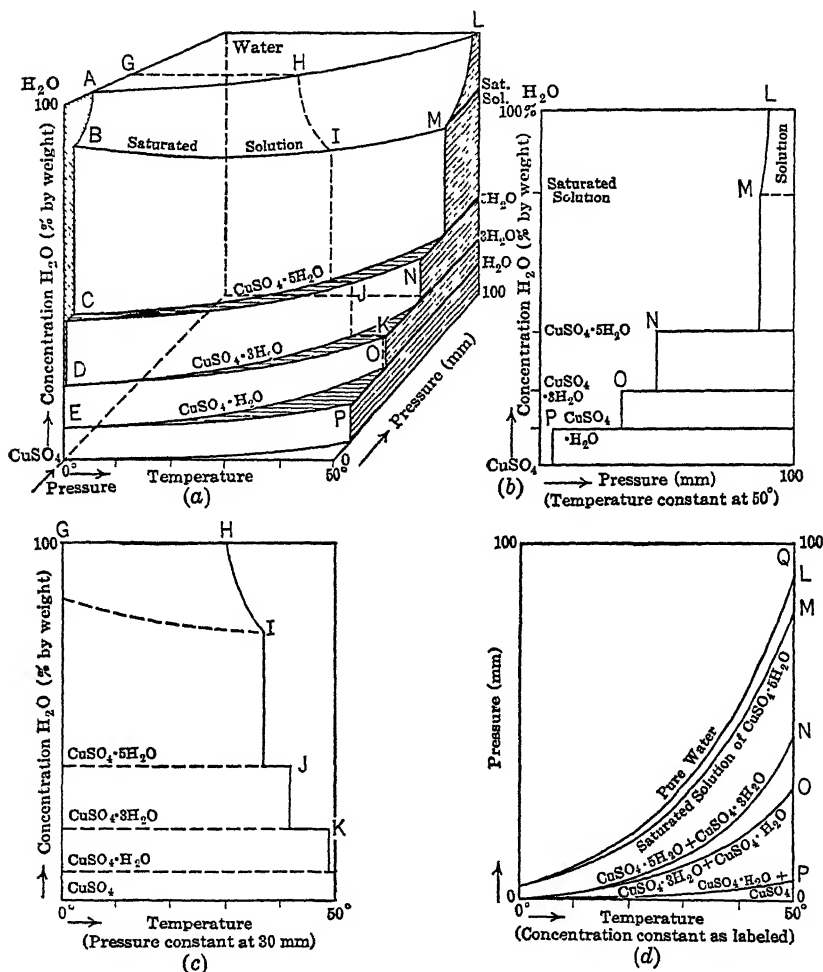
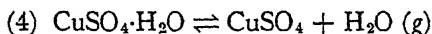
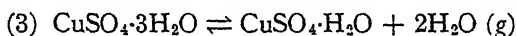
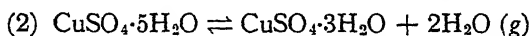


FIG. 84

drops to 4.5 mm., and remains constant until dehydration is complete. In practice the lines are less steep on account of slow diffusing of the water vapor.

The constant pressures observed in the dehydration correspond to the successive equilibria involved. The first equilibrium involves the pentahydrate, the saturated solution, and the vapor. After evapora-

tion of the liquid at 50° the pentahydrate, the trihydrate, and water vapor are in equilibrium at a pressure of 47 mm. which is maintained as long as any of the pentahydrate is present. When all the pentahydrate has disappeared, then the trihydrate begins to undergo dehydration into the monohydrate. This is a new equilibrium, and the pressure of the aqueous vapor remains constant at 30 mm., as long as any trihydrate remains. The last stage at 4.5 mm. corresponds to the equilibrium between the monohydrate, the anhydrous salt, and water vapor. The following equations represent the four successive equilibria:



Remembering that the pressure of the solids  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  are constant, an equilibrium constant may be written as follows:

$$K_p = p_{\text{H}_2\text{O}}^2$$

In a similar manner, it may be shown that the pressure of water vapor in the other equilibria must be constant. The observed pressure of the salt hydrates is definite and fixed only when three phases are present, for only under these conditions does an equilibrium exist.

Mixtures of two different crystalline salt hydrates are useful in establishing definite partial pressures of water. There are many different hydrated salts to choose from so that it is possible to obtain nearly any desired pressure. Sometimes the partial pressures of the anhydrous salt and the lowest hydrate are so low that they are used for dehydrating agents. Zinc chloride or calcium chloride is suitable. At 25° the mixture of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CuSO}_4$  has a partial pressure of 0.8 mm. of water and accordingly anhydrous copper sulfate will not take up any water at this temperature if the vapor pressure is less than 0.8 mm.

Of the three possible relations  $C$ - $P$ ,  $C$ - $T$ , and  $P$ - $T$  the temperature-concentration diagrams are most frequently used.

**Solubility of Salts.** When a solution is in equilibrium with a solid at a given temperature the solution is said to be *saturated* and the concentration of the saturated solution is known as the *solubility* of the salt at this temperature. The saturated solution may be prepared by agitating the solution with an excess of the finely divided solute



until there is no change in concentration on further standing. Again the solution may be mixed with an excess of the solute and its temperature changed to throw out of solution all the excess solute.

The solubilities of a few typical salts are given in Fig. 85, expressed in grams per 100 g. of water.

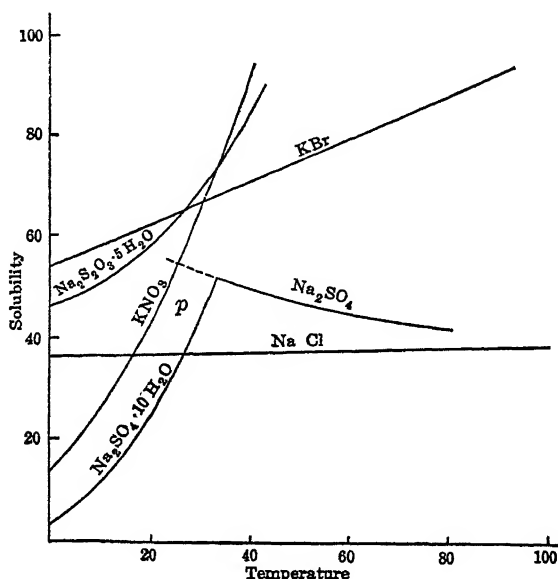


FIG. 85

The influence of temperature on the solubility depends on the differential heat of solution in the nearly saturated solution as predicted by the principle of Le Chatelier and laws of thermodynamics (page 139). Most salts absorb heat when dissolved, and accordingly they are more soluble at the higher temperatures, as is shown in Fig. 85 with potassium nitrate. If a salt evolves heat on solution, it decreases in solubility as the temperature is raised, as indicated for sodium sulfate above 32.38°. If the different factors are so balanced that heat is neither absorbed nor evolved, as is nearly true in a solution of sodium chloride in water, the solubility is almost unaffected by temperature. The greater the differential heat of solution the steeper is the solubility-temperature curve.

The dissolving of a solid in a liquid involves several factors. In ideal solutions the molecules break away from the crystal and fill the volume of the solvent until the solution is saturated, in the same way that molecules from a crystal fill an evacuated space. This proc-

ess absorbs heat corresponding to the heat of sublimation. Ideal solutions are rare; usually the molecules interact with the solvent or undergo ionization, and these effects may either absorb or evolve heat. The mere fact that the concentration in solution is usually much greater than the concentration in a previously evacuated space indicates that the solvent is exerting a special influence on the solute.

Solubility curves are usually continuous except when there is transition from one form to another. One solubility curve shown in Fig. 85 furnishes an illustration. At temperatures below  $32.38^{\circ}$  the dissolved salt is in equilibrium with the hydrated  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  which dissolves with the absorption of heat, but at temperatures above  $32.38^{\circ}$  the dissolved salt is in equilibrium with the anhydrous salt  $\text{Na}_2\text{SO}_4$  which dissolves with the evolution of heat. Accordingly the solubility of the hydrated salt increases with temperature, but above the transition temperature the solubility of the anhydrous salt decreases.

That these are two solubility curves is proved by the fact that the solubility curves of the hydrated and anhydrous salts in supersaturated solutions are continuations of the corresponding curves for saturated solutions, as shown by the dotted curve in Fig. 85. If any point is selected, such as  $p$  lying between the dotted curve and the full curve, it is apparent that it represents a solution supersaturated with respect to  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , but unsaturated with respect to  $\text{Na}_2\text{SO}_4$ . If pure anhydrous sodium sulfate is shaken with this solution it will dissolve slowly, whereas if a trace of the hydrated salt is added, the solution will deposit  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , until the amount remaining in solution corresponds to the solubility of the hydrate at that temperature.

Just as an increase in temperature increases the solubility of a salt which absorbs heat, so an increase in pressure increases the solubility of a salt which dissolves with a shrinkage in volume. The influence of pressure on solubility of a solid or liquid is quite small. It is stated by van't Hoff that the solubility of ammonium chloride, which gives an increased volume on solution, decreases by 1 per cent for 160 atm., whereas the solubility of copper sulfate, which gives a decreased volume on solution, increases by 3.2 per cent for 60 atm. These data are in agreement with the theorem of Le Chatelier and the second law of thermodynamics. Extensive work on the compressibilities of solutions has been done by Gibson.\*

The solubility of solids is somewhat dependent upon their state of division. Thus, Hulett† found that ordinary gypsum at  $25^{\circ}$  gives a saturated solution containing 2.080 g. of  $\text{CaSO}_4$  per liter, whereas,

\* Gibson, *J. Am. Chem. Soc.*, **57**, 284 (1935).

† Hulett, *J. Am. Chem. Soc.*, **27**, 49 (1905).

when very finely divided gypsum is shaken with this solution, it is possible to increase the content of dissolved  $\text{CaSO}_4$  to 2.542 g. per liter. Normally crystals are sufficiently large so that this phenomenon is not a factor.

When a saturated solution is cooled, every trace of solid solute being excluded, the excess of dissolved solid may not separate. Such a solution is said to be *supersaturated*. The explanation of supersaturation is probably to be found in the fact that the submicroscopic crystals which would normally be the first to deposit have a higher solubility and the crystallization process cannot easily get started. When an ordinary crystal of the solute with a normal solubility is introduced, however, the extra dissolved material crystallizes out immediately. The greater solubility of the very small crystals may, perhaps, be attributed to the existence of more isolated atoms or groups of molecules which can break away from the crystal more easily. This view is strengthened by the fact that if a mixture of large crystals and very small ones is allowed to stand the small ones disappear and the larger ones grow larger — a procedure which is followed in the digesting of precipitates in quantitative analysis to render them better suited for filtration.

Extremely small particles of crystals occurring, for example, as dust in a room, are sometimes sufficient to prevent supersaturation. Supersaturation can sometimes be relieved also by vibrations due to friction on glass or metal surfaces immersed in the solution.

**The Phase Rule.** In 1876 Professor J. Willard Gibbs\* of Yale University discovered a generalization known as the phase rule† which has been of great help in studying equilibria in heterogeneous systems. The phase rule together with his many important generalizations in thermodynamics have given Gibbs a position as one of the geniuses of science. Phase diagrams and the phase rule have been of great value in solving practical problems such as the recovery of alloys or salts from complicated mixtures and the adjustment of temperature, pressure, and composition to obtain a desired product. The extraction of potassium chloride from the Stassfurt salt deposits was one of the early examples. It should be pointed out that the phase rule applies only to systems which are in a state of equilibrium, that it does not predict new things, but that it is very valuable in correlating data. It may be used to state what type of relations may

\* Gibbs, *Trans. Conn. Acad. Sci.*, 1876-78.

† A brief derivation may be found in Findlay and Campbell "The Phase Rule and Its Applications," Longmans. Green and Co., New York, 1938.

be expected but the exact shape of the curves relating different variables must be determined by experiment.

In general, the phase rule is concerned with the number of variables which are involved in any system and with the number of relations between these variables. The ordinary variables are temperature and pressure and the concentration of materials in each of the phases. The fundamental statement of the phase rule is

$$F = C - P + 2 \quad [1]$$

where  $F$  is the number of degrees of freedom,  $C$  is the number of the components and  $P$  is the number of phases. These terms need further definition.

A phase has been defined before as a homogeneous region of uniform physical and chemical composition. In a system containing ice, liquid water, and water vapor in equilibrium there are three phases. It makes no difference how many pieces of ice are floating on the water; there is just one ice phase.

The number of components  $C$  is the minimum number of chemical constituents which must be specified in order to describe the composition of each phase present. In the system  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$  there are three chemical individuals but the number of components is only two because the three constituents are connected by an equilibrium. The simplest choice of components is  $\text{CaO}$  and  $\text{CO}_2$ , but  $\text{CaCO}_3$  and  $\text{CO}_2$ , or  $\text{CaCO}_3$  and  $\text{CaO}$  could be chosen; in the latter case the composition of the  $\text{CO}_2$  phase could be obtained by taking the difference between the  $\text{CaCO}_3$  and the  $\text{CaO}$ . In the system ice, water, and vapor, previously referred to, there is one component,  $\text{H}_2\text{O}$ . At very high temperatures there would be some oxygen and some hydrogen in equilibrium but at ordinary temperatures this dissociation is neglected.

The number of degrees of freedom  $F$  is the number of independent variables, temperature, pressure, and concentration in the different phases which must be specified in order to define the system completely. A mere change in the relative amounts of the phases present is not considered as a variable. Another definition of  $F$  is the number of variables which may be changed independently without causing the appearance or disappearance of a phase.

The greater the number of chemical substances present, the greater the number of variables. Since the presence of different phases gives added information about the system, it follows that the greater the number of phases the fewer are the variables which must be defined,

i.e., the fewer are the degrees of freedom  $F$ . The phase rule simply gives the quantitative relation between the variables  $F = C - P + 2$ . The number 2 is valid only if there are two variables, commonly temperature and pressure, in addition to concentration. If there is a third variable such, for example, as a magnetic field, the phase rule becomes  $F = C - P + 3$ . Again, if the conditions are so fixed that the pressure is not a variable and there is only one variable in addition to concentration, then  $F = C - P + 1$ .

Referring now to the one component system water shown in Fig. 83, it will be remembered that in the areas two variables, temperature and pressure, had to be stated in order to define the system completely. Here  $F = 2$ , because  $C = 1$  and  $P = 1$  and  $F = C - P + 2 = 1 - 1 + 2 = 2$ . Along any of the lines, if one variable is specified, it was shown that the condition of the system is completely defined. There are two phases along a line. Then  $F = C - P + 2 = 1 - 2 + 2 = 1$ . At the point  $O$  there are three phases and so  $F = C - P + 2 = 1 - 3 + 2 = 0$ . It was shown that at this point the conditions are completely fixed. Neither temperature nor pressure can be altered without losing one of the three phases, i.e., there are no degrees of freedom.

**The System Sulfur (Rhombic, Monoclinic), Liquid, and Vapor.** This one-component system is complicated because there are two solid phases, in addition to the liquid and vapor phases. At ordinary temperatures, rhombic sulfur is the stable modification. When it is heated rapidly it melts at  $115^\circ$ , but if maintained in the neighborhood of  $100^\circ$  it gradually changes into monoclinic sulfur, which melts at  $120^\circ$ . Monoclinic sulfur can be kept indefinitely at  $100^\circ$  without undergoing change into the rhombic modification; in other words, it is the stable phase at this temperature. It is evident, therefore, that there must be a temperature above which monoclinic sulfur is the stable form, and below which rhombic sulfur is the stable modification. This temperature, at which two different crystalline modifications are in equilibrium with each other, and with their vapor is termed the *transition temperature*. The transition temperature for rhombic and monoclinic sulfur is sharp and occurs at  $95.6^\circ$ . The change from one form into the other is relatively slow, so that it is possible to measure the vapor pressure of rhombic sulfur up to its melting point, and that of monoclinic sulfur below its transition point. The vapor pressure of solid sulfur at ordinary temperature is small, but measurable.

The complete pressure-temperature diagram for sulfur is shown in Fig. 86. At the point  $O$ , rhombic and monoclinic sulfur are in

equilibrium with sulfur vapor, this being a triple point, analogous to the point  $O$ , in Fig. 83. The vapor-pressure curves of rhombic and monoclinic sulfur are represented by  $OB$  and  $OA$ , respectively. The curve  $OA'$ , which is a continuation of  $OA$ , is the vapor-pressure

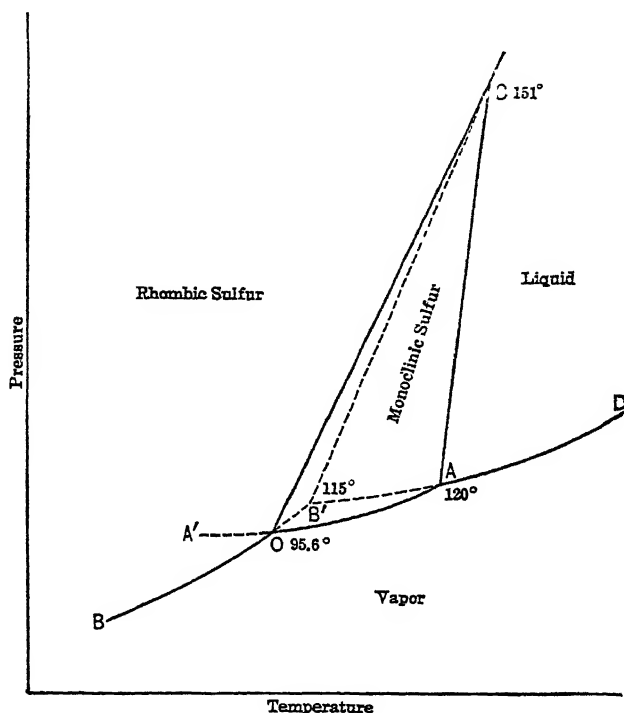


FIG. 86

curve of monoclinic sulfur in a metastable region. In like manner,  $OB'$  represents the vapor-pressure curve of rhombic sulfur in the metastable condition,  $B'$  being a metastable melting point. As in the pressure-temperature diagram for water, the metastable phases have the higher vapor pressure. The effect of increasing pressure on the transition point  $O$  is represented by the line  $OC$ . Since increase in pressure raises the transition point, the line  $OC$  slopes away from the vertical axis. The effect of increasing pressure on the melting point of monoclinic sulfur is shown by the curve  $AC$ . It also slopes away from the vertical axis, but the change in the melting point of monoclinic sulfur produced by a given change in pressure is less than the corresponding change in the transition point and so the two curves,  $OC$  and  $AC$ , intersect at the point  $C$ . This point corresponds to a

temperature of  $151^\circ$  and a pressure of 1280 atm. The vapor-pressure curve of stable liquid sulfur is represented by the curve  $AD$ . The vapor-pressure curve of the metastable liquid phase is represented by the curve  $AB'$ , which is continuous with  $AD$ . The dotted line  $B'C$  represents the effect of pressure on the metastable melting point of rhombic sulfur. Monoclinic sulfur does not exist above the point  $C$ . Hence, when liquid sulfur is allowed to solidify at pressures exceeding 1280 atm., the rhombic modification is formed, whereas under ordinary pressures the monoclinic modification appears first.

The phase rule enables one to state the exact conditions required for equilibrium, and to check the results of experiment. Thus, according to the formula,  $C - P + 2 = F$ , since  $C = 1$ , the system will be non-variant when  $P = 3$ . Four phases are involved, and, theoretically, any three of these may be coexistent. Thus four triple points are possible as follows:

- (1) Rhombic sulfur, monoclinic sulfur, and vapor ( $O$ ).
- (2) Rhombic sulfur, monoclinic sulfur, and liquid ( $C$ ).
- (3) Rhombic sulfur, liquid, and vapor ( $B'$ ).
- (4) Monoclinic sulfur, liquid, and vapor ( $A$ ).

In this particular system all four possible triple points can be realized experimentally, because the transition from one form to the other is slow.

As in the case of water, the lines in Fig. 86 represent univariant systems and the areas represent bivariant systems. It is a good exercise to tabulate the univariant and bivariant systems represented in Fig. 86.

**Two-Component Systems.** In two-component systems the following table summarizes the phase rule relations.

TABLE I  
PHASE RULE RELATIONS FOR A TWO-COMPONENT SYSTEM

Number of Phases	Possible Variables	Number of Variables	Number of Degrees of Freedom $F = C - P + 2$	Relations Which May Be Deduced
1	$p, T, X_A^I$	3	3	All the variables are independent.
2	$p, T, X_A^I, X_A^{II}$	4	2	Two independent variables.
3	$p, T, X_A^I, X_A^{II}, X_A^{III}$	5	1	Only one variable may be chosen independently.
4	$p, T, X_A^I, X_A^{II}, X_A^{III}, X_A^{IV}$	6	0	All variables are fixed.

The subscripts refer to the component and the superscripts to the phase. Thus  $X_A^{\text{II}}$  signifies the concentration of  $A$  in the phase II. Inasmuch as the maximum number of variables is three, the system may be represented by a space model as in Fig. 84 for the system  $\text{CuSO}_4$  and  $\text{H}_2\text{O}$ .

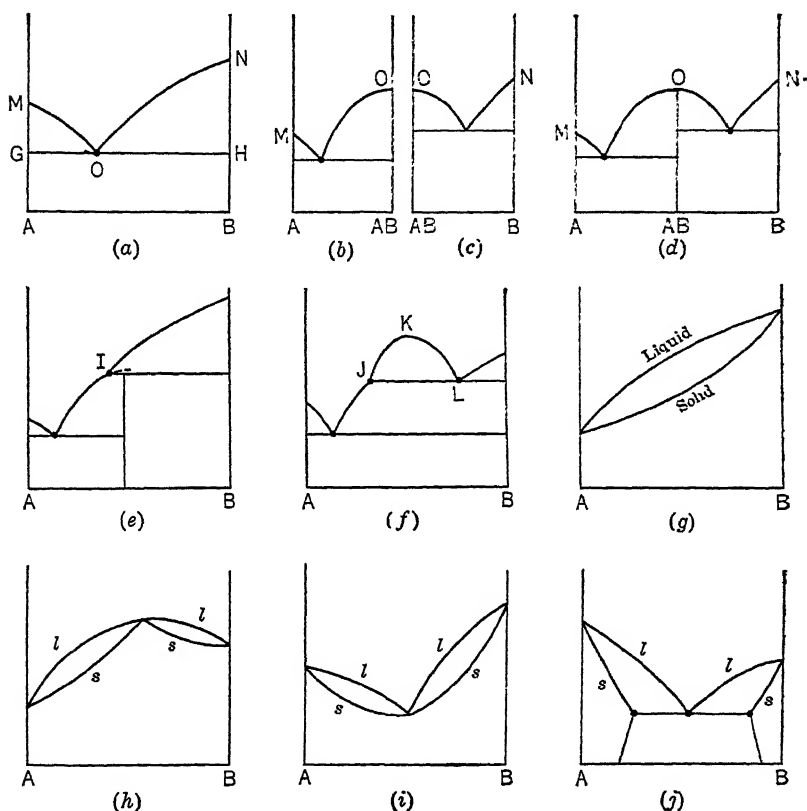


FIG. 87

Since three-dimensional models of this type are difficult to construct and use, the two-dimensional graphs representing sections of the space model are usually employed. The significance of these sections was illustrated in Fig. 84. Of the three possible planes  $P-C$ ,  $P-T$ , and  $T-C$ , the temperature-composition plane diagrams are much the most common. Several important types of two component systems are illustrated in Fig. 87 in which temperature is plotted vertically and composition horizontally;  $A$  represents 100 per cent of one component and  $B$  represents 100 per cent of the other. The composition is given



in per cent by weight; or, more significantly, in mole per cent or mole fractions. The space above the uppermost lines represents liquid solution, and along these lines a new solid phase or phases separate. The fixed pressure is taken high enough to condense all the vapor so that the diagrams refer to condensed systems containing only solid and liquid phases. Then by the phase rule

$$F = C - P + 1 \quad [2]$$

In Fig. 87*a* the freezing point of pure *A* is shown at *M*. Along the line *MO* pure solid *A* is separating out from the solution. The point *N* represents the freezing point of pure *B* and along the line *NO* pure solid *B* is separating. At *O* both pure solid *A* and pure solid *B* appear together. This is known as the *eutectic temperature*.

The phase rule is powerless to predict the curves *MO* and *NO* or the position of *O*. They must be determined by experiment. The phase rule, however, shows that in the area above *MON*, temperature and composition may be varied without changing the number of phases because  $F = C - P + 1^* = 2 - 1 + 1 = 2$ . Along *MO* or *NO* fixing either the temperature or the composition of the solution defines the system. Then  $F = 2 - 2 + 1 = 1$ .

At the point *O*,  $F = 2 - 3 + 1 = 0$  and if any change is made in concentration or temperature, one of the two solid phases or the liquid phase will disappear. In the area *AGHB* there are the two solid phases *A* and *B*. In the area *GOM* there are two phases, solid *A* and liquid solution, whereas in *HON* there is solid *B* and liquid solution.

Figures 87*b* and *c* help to explain Fig. 87*d*. Figure 87*b* is just like Fig. 87*a* except that a compound of *A* and *B*, namely, *AB*, takes the place of *B*. The freezing point of *AB* is lowered by adding *A* to the solution. The pure solid *AB* separates when the solution is cooled. Figure 87*c* is similar to Fig. 87*a* except that *AB* takes the place of *A* and its freezing point is lowered by additions of *B*. When these two parts, *b* and *c*, are pushed together we have Fig. 87*d* which is typical of two-component systems in which a compound is formed. In general, a maximum in a temperature-composition curve, in which solids separate from the liquid phase on cooling, indicates the formation of a chemical compound, and the composition at which this maximum occurs is the composition of the solid compound. It corresponds to a stoichiometric ratio such as *AB*, *AB*<sub>2</sub>, *AB*<sub>3</sub>, *A*<sub>2</sub>*B*<sub>5</sub>, etc. In studying a system of this kind it is best to draw vertical lines down

\* The pressure is fixed.

from the maximum as shown and consider the diagram as two separate diagrams as in Figs. 87*b* and *c*. If the compound dissociates extensively in solution the maximum is rather flat on top, and if it dissociates but slightly, the approaches to the maximum are steep.

Figure 87*e* illustrates a special case of compound formation in which the freezing point of one of the components is so far above that of the compound that its freezing-point curve intersects the freezing-point curve of the compound on the opposite side of the maximum. The maximum can be attained only under condition of unstable equilibrium. Above the break at *I* pure *B* separates and below it the compound *AB*. Such a point is sometimes called an incongruent melting point.

Figure 87*f* illustrates the case in which two liquid phases are involved. The freezing point of *A* is lowered by the addition of *B* and the freezing point of *B* is lowered by the addition of *A* as shown at the extreme ends of the diagram. Along the line *JK* the liquid phase consists of *A* saturated with *B* and along the line *KL* the liquid phase consists of *B* saturated with *A*, and these two saturated phases do not mix with each other. The point *K* does not correspond to any particular compound or ratio. At temperatures above *K* only one liquid phase is possible no matter what the composition. In the area *JKL* two liquid phases exist. An example of this type of diagram was shown in Fig. 61 on page 194.

The remaining Figs. 87 *g-j* apply to two component systems in which the two solids are soluble in each other. They will be discussed in a later section. The solid separating on cooling is not a pure substance but a solution of one substance in the other, the exact composition of the separating phase depending on that in the liquid phase. In Figs. 87*g*, *h*, and *i* there is complete solubility of the solid phases but in Fig. 87*j* the solubility is limited so that two different solid solutions giving two separate phases can exist side by side.

**Cooling Curves.** Cooling curves may be used in the method of thermal analysis to construct phase diagrams. It is convenient particularly for alloys where the chemical analysis of the separating phases is difficult on account of the contaminating liquid. A mixture of known composition is weighed out and heated until all is liquefied. Then it is allowed to cool and the temperature is recorded at frequent intervals as read on a thermometer or thermocouple. A smooth cooling curve is plotted from the data, but whenever a solid phase separates, heat corresponding to the heat of fusion is evolved and this offsets fully or in part the heat being lost from the melted material and container. The rate of cooling, i.e., the slope of the line, becomes less,

and the temperature at which an inflection point or plateau occurs can be used in plotting the phase diagram.

This method is illustrated in Fig. 88 for the bismuth-cadmium system. The cooling curve for pure bismuth indicated by 0 per cent cadmium is shown at the extreme left. The liquid cools off along  $AB$  but when  $B$  is reached solid bismuth appears and the temperature

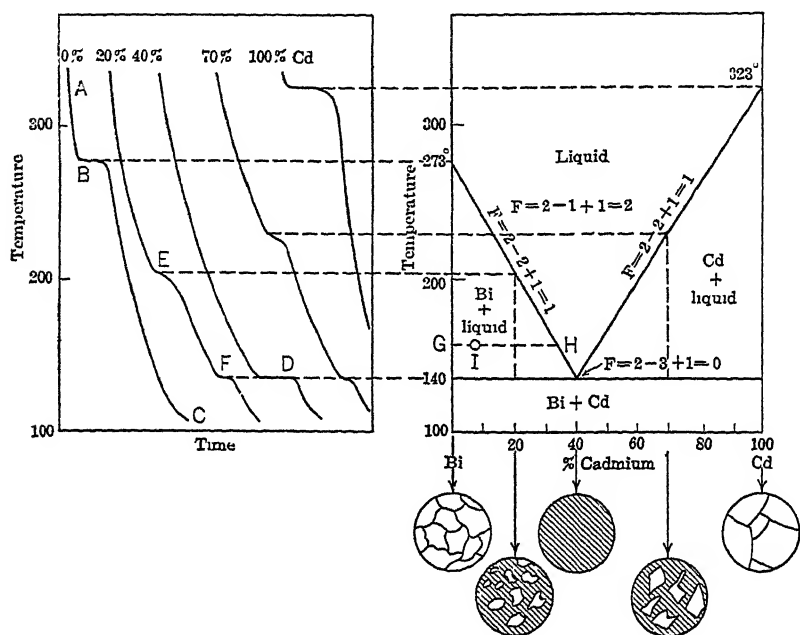


FIG. 88

remains stationary at 273° until all the liquid has solidified. The cooling curve of the solid bismuth is shown along the line  $BC$ . A similar curve for the freezing point of pure cadmium is indicated by the line marked 100 per cent cadmium, which indicates a freezing point at 323°. The line marked 40 per cent shows a single plateau  $D$  which corresponds to the eutectic point at 140°, where both solid bismuth and solid cadmium are coming out together and evolving heat. Other compositions show two changes in curvature, a sharp plateau at the eutectic point, and a more gradual nick in the curve at a higher temperature. In the mixture containing 20 per cent cadmium, pure bismuth starts to solidify from the solution at  $E$ . As it does so the remaining solution becomes more concentrated in cadmium and the freezing point is lowered gradually as the composition changes.

Finally at  $F$  solid cadmium as well as solid bismuth separates out and the whole system goes solid. The system consists of 80 per cent solid bismuth and 20 per cent solid cadmium just as the original liquid system consisted of 80 per cent and 20 per cent of the liquids.

These freezing points and the eutectic point are then transferred as shown by dotted horizontal lines to the diagram at the right in which the temperatures are plotted against the compositions of the corresponding mixtures.

**The System Bismuth-Cadmium.** In the phase diagram shown at the right of Fig. 88 temperature and composition are the only variables; the pressure is assumed to be fixed and at a value high enough so that all the vapor is condensed, giving only solid and liquid phases. Then  $F = C - P + 1 = 2 - P + 1$ . The number of components, phases, and degrees of freedom are marked at significant areas, lines, and points.

Below the eutectic point the two solids bismuth and cadmium are present. In this region there are two components and two phases, pure bismuth and pure cadmium so  $F = 2 - 2 + 1 = 1$ . The compositions of each phase are known and the only variable is the temperature which gives the one degree of freedom to the system. As explained before, the pressure is fixed and the vapor phase is considered negligible. In any mixture, cooled below the eutectic temperature, the solid which separates will have crystals of both bismuth and cadmium. When the eutectic mixture solidifies the solid may appear to be different because it is fine-grained, but it is not to be regarded as a new phase. It is still a physical mixture of *two* phases, solid bismuth and solid cadmium. The different solidified mixtures would have an appearance under the microscope somewhat similar to that indicated in the circles.

In the region labeled Bi + liquid there are two separate phases, solid bismuth, and liquid solution. There is one degree of freedom ( $F = 2 - 2 + 1 = 1$ ) and the system is completely defined as soon as the temperature or the composition of the liquid phase is specified. As one passes along a horizontal line (i.e., isothermal),  $GIH$ , the ratio of solution of composition  $H$  to pure solid bismuth, gradually increases. At the point  $I$ , for example, the ratio of bismuth to liquid of composition  $H$  is equal to  $IH/IG$ . The composition of the liquid does not change, however, and along the line  $GIH$ ,  $F = 0$  because the temperature as well as the pressure is fixed. The composition of the total system will change as the relative amounts of  $G$  and  $H$  change, but the amounts of material in the total system does not constitute a

phase rule variable. It is the concentration of material in a given phase that is significant.

**Systems Exhibiting Chemical Interaction.** In the temperature-concentration diagram given in Fig. 89, a maximum is shown in the liquid-solid curve and so it may be concluded that the zinc and mag-

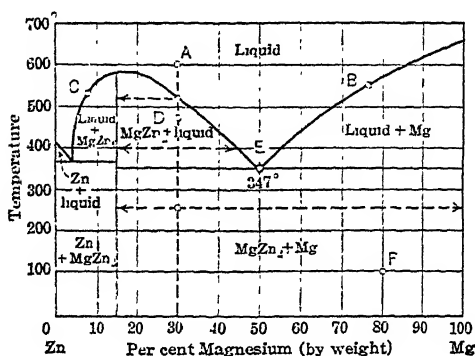


FIG. 89

nesium interact to give a chemical compound. The compound has the formula  $MgZn_2$  and it melts at  $575^\circ$ . There is one eutectic point at  $368^\circ$  with Zn and  $MgZn_2$  separating out together and another at  $347^\circ$  with Mg and  $MgZn_2$  freezing simultaneously. The diagram is split into two by passing a vertical line through the maximum and the same conditions apply that applied to Fig. 88 and Fig. 87d. The pressure is fixed and only solid and liquid phases are represented. It is assumed that the pressure is high enough to condense all the vapor.

*Example 1.* State what phases are present at A, B, C, D, E, and F, and give the number of degrees of freedom. There are two components and the pressure is fixed.

PHASES	DEGREES FREEDOM
	$C - P + 1 = F$
A Liquid	$2 - 1 + 1 = 2$
B Liquid, solid Mg	$2 - 2 + 1 = 1$
C Liquid, solid $MgZn_2$	$2 - 2 + 1 = 1$
D Liquid, solid $MgZn_2$	$2 - 2 + 1 = 1$
E $MgZn_2$ , Mg, liquid	$2 - 3 + 1 = 0$
F $MgZn_2$ , Mg	$2 - 2 + 1 = 1$

In the region D it is sufficient to fix either temperature or concentration of the liquid phase. The ratio of  $MgZn_2$  to liquid is not a variable because the concentration in the phases is all that counts in the phase rule, and this is fixed when either temperature or composition is fixed.

*Example 2.* Seventy grams of zinc and 30 g. of magnesium are heated to  $600^{\circ}$  giving the point *A* in Fig. 89. Describe what happens when this total mixture is cooled down to  $0^{\circ}$  as indicated by the vertical, dotted line. (The experiment would have to be done in an inert atmosphere to prevent oxidation by air). At  $520^{\circ}$  solid  $\text{MgZn}_2$  separates out as indicated by the top arrow; the remaining solution becomes richer in the solute magnesium; the temperature falls still lower and more solid  $\text{MgZn}_2$  is thrown out of solution. The freezing point is gradually lowered as the solution becomes richer in Mg. At  $400^{\circ}$  a considerable amount of  $\text{MgZn}_2$  has come out of solution leaving a solution of 42 per cent magnesium and 58 per cent zinc as indicated by the arrows. Finally at  $347^{\circ}$ , when the liquid has become 49 per cent magnesium and 51 per cent zinc, the whole solution freezes, solid  $\text{MgZn}_2$  and solid Mg coming out together.

From this temperature down to  $0^{\circ}$  there is no further change in composition or phases. At all temperatures below  $347^{\circ}$  there is pure Mg and  $\text{MgZn}_2$ . The ratio of the amounts of the two is  $\text{MgZn}_2/\text{Mg} = (100 - 30)/(30 - 15) = 4.67$ .

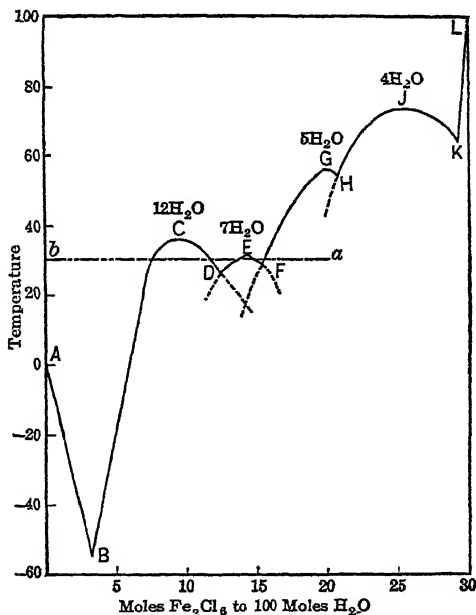


FIG. 90

Many interesting phase diagrams are found among the solutions of electrolytes in water. The concentration-temperature diagram for ferric chloride and water, plotted from Roozeboom's data, is given in Fig. 90. The freezing point of pure water is represented by *A*, and the lowering of the freezing point produced by the addition of ferric

chloride is indicated by the curve  $AB$ . At the eutectic temperature,  $-55^\circ$ , ice,  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ , and saturated solution are in equilibrium, and the system is nonvariant.

When salts and water freeze out together, the eutectic temperature is sometimes called a cryohydric temperature and a eutectic mixture with the aqueous salt solution is called a cryohydrate. The pressure is fixed high enough so that all the vapor is condensed, leaving only liquid phase and the two solid phases. Then for a eutectic or cryohydrate,  $F = C - P + 1 = 2 - 3 + 1 = 0$ . When first discovered these cryohydrates were thought to be chemical compounds, but the lack of homogeneity can be detected under the microscope. Furthermore, the constituents are seldom present in simple molecular proportions.

On the addition of more ferric chloride, the ice phase disappears, and the univariant system,  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ , and saturated solution, is obtained. The equilibrium is represented by the curve  $BC$ , which may be regarded as the solubility curve of the dodecahydrate. On continuing the addition of ferric chloride, the temperature of equilibrium rises until the point  $C$  is reached. Here the composition of the solution is identical with that of the dodecahydrate, and the temperature corresponding to this point,  $37^\circ$ , may be looked upon as the melting point of  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ .

Further addition of ferric chloride naturally lowers the melting point, and the equilibrium changes as shown along the curve  $CD$ . It is thus possible to have two saturated solutions at the same temperature, one of which contains more water and the other less than the hydrate which is in equilibrium with the solution. At the point  $D$ , the curve reaches another minimum, at which there is equilibrium between the dodecahydrate, the heptahydrate, and saturated solution. The system is non-variant.

On further addition of ferric chloride, another maximum is reached at  $E$ , corresponding to the melting point of the heptahydrate. In a similar manner, two other maxima at greater concentrations of ferric chloride reveal the existence of the hydrates  $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$  and  $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ . At the three remaining points the following phases are in equilibrium: at  $F$ ,  $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$ , and saturated solution; at  $H$ ,  $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ , and saturated solution; and at  $K$ ,  $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{Cl}_6$ , and saturated solution. The solubility of the anhydrous salt is represented by the curve  $KL$ . Metastable solubility is given by dotted lines. If vapor is considered, pressure is a variable and  $F = C - P + 2$ .

If a dilute solution of ferric chloride is evaporated at  $31^\circ$  ( $E$  is  $32.5^\circ$  and  $F$  is  $30.0^\circ$ ) the water disappears, and a residue of dodecahydrate

remains. This residue then liquefies, and again dries down, the composition of the residue corresponding to the heptahydrate: on further evaporation, the phenomenon is repeated, the residue corresponding to the pentahydrate. The dotted line, *ab*, shows the isothermal along which the composition varies. It would have been a difficult matter to explain the alternations of moisture and dryness, observed in this experiment, without the concentration-temperature diagram.

**Solid Solutions.** In aqueous solutions and in most common solutions in the laboratory the solvent freezes out as a pure solid. However, there are many solutions in which the solid solvent which freezes out contains the solid solute dissolved in it. An example is a solution of iodine dissolved in benzene. When the temperature is lowered to about 5° the crystals of benzene which freeze out are colored with iodine and the amount of iodine dissolved in the solid is proportional to the amount of iodine dissolved in the liquid solution. There is a distribution of iodine between the liquid and solid phases just as there is distribution between two immiscible solvents, as shown in Table II.

TABLE II  
DISTRIBUTION OF IODINE BETWEEN LIQUID AND SOLID BENZENE

$c_1$ in Liquid Benzene	$c_2$ in Solid Benzene	$c_2/c_1$
3.39	1.279	0.377
2.587	0.925	0.358
0.945	0.317	0.336

One of the characteristic properties of a dissolving solute is its tendency to diffuse into the pure solvent. Solids also have the property of mixing by diffusion. Thus, by keeping gold and lead in contact at constant temperature for four years, gold was detected in the layer of lead at a distance of 7 mm. from the surface of separation. Many other instances of diffusion in solids have been observed.

Certain natural silicates, the so-called zeolites, are transparent and homogeneous. Since they contain varying quantities of water they may be regarded as examples of solutions of liquids in solids. This classification is further justified by the fact that portions of the water may be removed and replaced by other substances, such as alcohol, with apparently no change in the transparency or homogeneity of the mineral.

The existence of these solid solutions introduces complications in the



study of phase diagrams as indicated in Figs. 87g-j. Two-component systems which have solid solutions consist of *two* solutions, one a *liquid solution* and the other a *solid solution*, in equilibrium with each

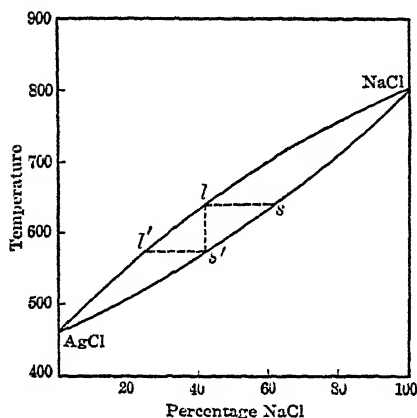


FIG. 91

other. Obviously, the complete temperature-concentration diagram must contain two curves. In Fig. 91 for a mixture of silver chloride and sodium chloride the upper curve, which corresponds to the liquid solution, is called the crystallization-point curve and the lower curve, which corresponds to the solid solution, is known as the melting-point curve. The region above the upper curve represents liquid solutions; the region below the lower curve represents solid solutions. The space between the two curves represents mixtures of liquid and solid phases in varying proportions. If the temperature of a fused mixture of these two salts, having the composition represented by the point *l* on the crystallization-point curve, is gradually lowered, the first solid phase to separate out will have the composition represented by *s*. If the temperature is lowered very slowly, so as to ensure the homogeneity of the solid phase, the composition of the final portion of the solution to solidify corresponds to that of the point *l'*, and the composition of the solid with which it is in equilibrium is represented by *s'*. If the solution is cooled rapidly, the solid phase will not become homogeneous, owing to the slow rate of diffusion of the two components in the mixture, and consequently the final temperature of solidification will be considerably lower than that corresponding to the point *s'*. The rate of cooling is of great practical importance in connection with the preparation of alloys, where the rate of diffusion of the constituents is necessarily slow.

The system mercuric bromide-mercuric iodide shown in Fig. 92 exhibits a minimum. Another type of solid solution which exhibits a maximum was shown in Fig. 87h. These curves are analogous to the three types of boiling-point curves of binary mixtures which have been discussed in an earlier chapter (page 185). In both cases there is equilibrium at a given temperature between solutions in two different phases.

A large number of binary systems are known in which the two components do not form a continuous series of mixed crystals. This case, which is perfectly analogous to that of the partial miscibility of liquids, may be illustrated by the system  $\text{KNO}_3\text{-TlNO}_3$ , a diagram of which is shown in Fig. 93. At the temperature corresponding to *C*, two solid solutions having compositions corresponding to *D* and *E* separate out, the temperature remaining constant until all the liquid has solidified. On lowering the temperature below *C*, the two solid solutions, which were in equilibrium at *C*, undergo a change in composition, as indicated by the dotted lines.

The area above *C* contains liquid of varying compositions and temperatures. The area at the left of *D* contains solid solutions of thallium nitrate in potassium nitrate of varying compositions and temperatures. In the area between *l* and *s* there are two phases, liquid solution and the saturated solid solution of  $\text{TlNO}_3$  in  $\text{KNO}_3$ , the composition of which is given by the line *s*. The concentration of both the liquid and the solid solution changes with the temperature.

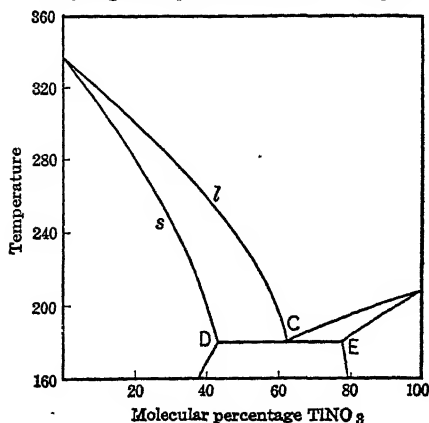


FIG. 93

tions, the composition of each at a given temperature being given by the lines extending below *D* and *E*.

**Alloys.** Phase diagrams have been of great help in understanding the behavior of mixtures of metals and in developing alloys with special properties. Freezing-point-concentration curves are particu-

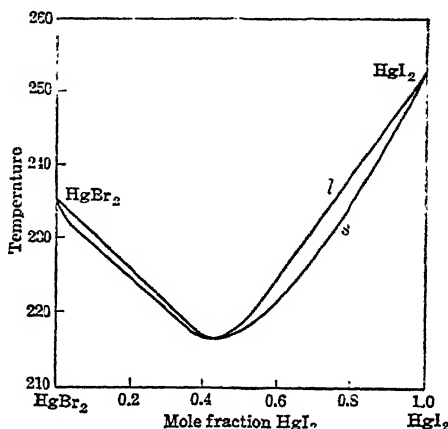


FIG. 92

At *C* there are three phases, liquid, solid  $\text{KNO}_3$  saturated with  $\text{TlNO}_3$  of composition *D*, and solid  $\text{TlNO}_3$  saturated with  $\text{KNO}_3$  of composition *E*.

In the area below *DCE* there are these two solid solu-

larly useful. The presence of a maximum in the curve shows that a chemical compound is produced by the combination of the two metals. If there is a single eutectic point without maxima, each of the two components separates from the liquid mixture in the pure state. The presence of solid solutions is indicated when there are two curves, one for melting, one for crystallization.

The hardening and tempering of steel involves the existence of solid solutions of carbon in different iron-carbon compounds. The

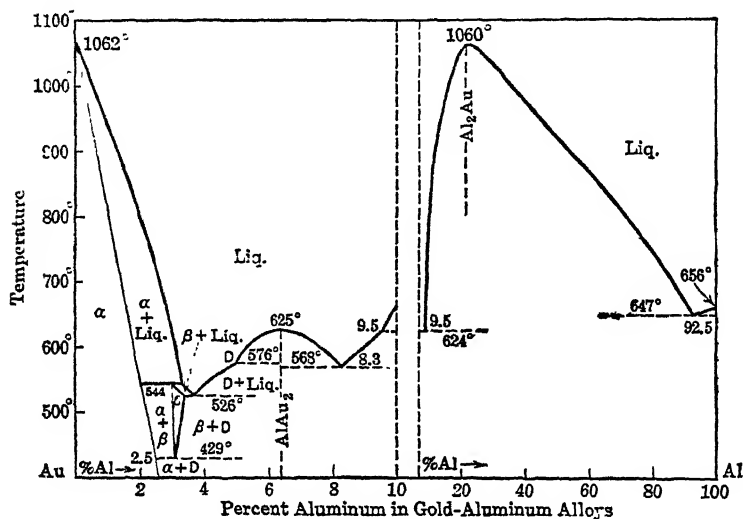


FIG. 94

solid solution stable at the high temperatures is hard and steel of the proper composition and temperature as given by the phase diagram will produce hard steel if it is quenched quickly in water or oil so that it does not have time to give the solid solution stable at the lower temperature. By heating up again to a somewhat lower temperature, opportunity is given for partial conversion to the softer solid solution which is stable at the lower temperature. In this way the steel may be given different degrees of hardening.

The temperature-composition diagram for mixtures of gold and aluminum is shown in Fig. 94.\* It illustrates a more complicated alloy in which several definite chemical compounds are formed. It is similar in character to the ferric chloride-water system shown in Fig. 90. The different compounds are indicated on the diagram, and

\* This figure is taken from International Critical Tables, Vol. II, p. 402 (1927), with permission of the publishers, McGraw-Hill Book Co.

it is evident that some of the maxima are obscured by overlapping curves. The pure compounds which correspond to the extrapolated maxima must exist only in a metastable state. There are also solid solutions of limited solubility similar to those shown in Fig. 43.

**Three-Component Systems.** Triangular coordinates are convenient for representing the composition of a system of three components where all three must add up to 100 per cent, because, within an equilateral triangle, the sum of the three distances drawn from a point

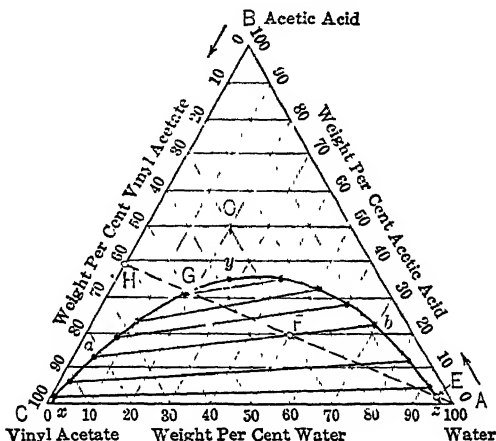


FIG. 95

parallel to the three sides, is equal to the side of the triangle. In Fig. 95 this type of diagram is used for the condensed system water, acetic acid, and vinyl acetate at 28° and constant pressure.\* The point O, for example, represents the composition 20 per cent water, 50 per cent acetic acid, and 30 per cent vinyl acetate.

When vinyl acetate is added to water a homogeneous solution is formed, provided that the amount of vinyl acetate does not exceed that corresponding to complete saturation, represented by the point *z*. If further amounts of vinyl acetate are added, the mixture will separate into two layers, one of which consists of a saturated solution of water in vinyl acetate, and the other, a saturated solution of vinyl acetate in water. The composition of these two immiscible solutions is represented by the points *x* and *z*.

If acetic acid, which dissolves completely in both liquids is added, it renders the water more soluble in the vinyl acetate and the vinyl acetate more soluble in the water. It distributes itself between the two

\* Smith, *J. Phys. Chem.*, **45**, 1301 (1941).

layers, forming two immiscible, ternary solutions of vinyl acetate, water, and acetic acid which are in equilibrium with each other. These solutions are represented by two points such as *a* and *b* within the triangular diagram. The line joining *a* and *b* is known as a *tie line*. Other tie lines are shown for other compositions; usually they are not parallel to the base *AC* of the triangle. The compositions of the two phases corresponding to the intersection of the tie lines with the curves *xy* and *zy* have to be determined experimentally. As more and more acid is added, the tie lines become shorter and shorter, and ultimately, when the compositions of the two solutions become identical, they shrink to the single point *y*. The point *y* is a *critical point*, since further addition of acetic acid will result in the formation of a single homogeneous phase. Any point under the curve represents a ternary mixture which will separate into two liquid phases; any point above the curve represents a single homogeneous liquid phase.

A ternary mixture whose composition is represented by the point *F* will separate into two conjugate ternary solutions having the compositions *a* and *b*. If a line is drawn from *A* through *F* cutting the isotherm *xyz* at *E* and *G* and the line *BC* at *H*, it can be shown that, in all mixtures represented by points on *AG*, the ratio of the components, *C/B*, is constant and equal to *HB/HC*. If to a mixture of vinyl acetate and acetic acid whose composition is represented by the point *H*, increasing amounts of water are added, there is obtained in succession: (1) a series of homogeneous solutions between *H* and *G*, (2) a series of heterogeneous mixtures of two conjugate solutions between *G* and *E*, and (3) another series of homogeneous solutions between *E* and *A*.

Owing to the fact that acetic acid does not distribute itself equally between water and vinyl acetate the critical point *y* lies below the highest point of the curve.

Vinyl acetate and water become more soluble at higher temperatures and the region where there are two immiscible phases would be smaller. The line *xyz* would fall below its present position at higher temperatures.

In applying the phase rule to these triangular diagrams, it must be remembered that the pressure and the temperature are fixed, and in most diagrams the vapor is condensed. Then  $F = C - P + O = 3 - P$ .

The percentage compositions *X* of two of the components provide the only variables, but these may apply to several different liquid phases.

When there is but one liquid phase, as in Fig. 95 above  $xyz$  there are two degrees of freedom, namely,  $X_A$  and  $X_B$  (or  $X_B$  and  $X_C$ , or  $X_A$  and  $X_C$ ), where  $A$ ,  $B$ , and  $C$  are the components. When there are two liquid phases, there are four possible variables; the percentage composition of two components in the water phase and the percentage composition of two components in the vinyl acetate phase. However, according to the phase rule only one of these variables is independent when there are two phases since  $F = 3 - 2 = 1$ . Referring to the line  $xyz$  on the triangular diagram, as soon as the percentage of water in one phase is specified, the system is completely described. For example, if on the line  $xyz$  the water is specified as 5 per cent giving the point  $a$ , the composition of vinyl acetate and acetic acid in this vinyl acetate layer is easily obtained from the triangle. Moreover, the percentage of each of the three components in the second liquid phase, the water phase, is determined by point  $b$  which lies at the other end of the tie line.

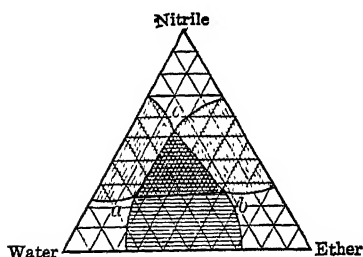


FIG. 96

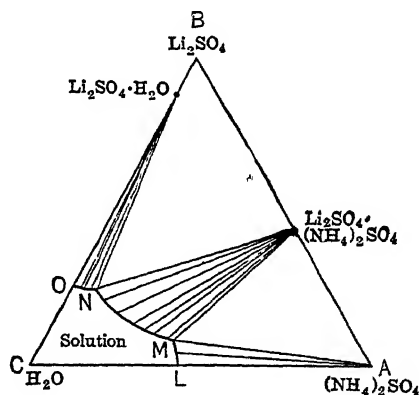


FIG. 97

The system water-ether-succinic nitrile furnishes an example of a three-component system containing three pairs of partially miscible liquids. This system at a particular temperature and pressure is represented in the diagram shown in Fig. 96. The compositions of all mixtures forming single homogeneous solutions are represented by points in the unshaded areas of the triangular diagram. All points lying within the single shaded areas represent mixtures which form two liquid layers; all points included within the triangular area  $abc$  represent mixtures which break up into three liquid layers of the composition  $a$ ,  $b$ , and  $c$ . All these compositions are fixed at a given temperature and pressure so that  $F = 0$ .

A common type of phase diagram is shown in Fig. 97. Here two different salts and water are given at the three apices of the equilateral triangle. The area at the left of the curves represents unsaturated solution. The solubility of pure  $(\text{NH}_4)_2\text{SO}_4$  in per cent at  $30^\circ$  is given by  $L$ ; and the solubility of pure  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  is given by  $O$ . The line  $LM$  shows how the solubility of  $(\text{NH}_4)_2\text{SO}_4$  is decreased by the addition of  $\text{Li}_2\text{SO}_4$  and the line  $ON$  shows how the solubility of  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  is changed by the addition of  $(\text{NH}_4)_2\text{SO}_4$ . Along the line  $MN$  a double salt  $\text{Li}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$  precipitates out. The tie lines give the composition of the solution which is in equilibrium with the salt for any total composition specified within these areas.

It is possible to represent temperature as a variable in a three component system using a triangular prism in which the temperature is plotted at right angles to the base of the prism. Such prisms are useful in determining the composition of a three-metal alloy which will give the lowest possible melting point. Low-melting alloys are used, for example, in automatic water sprinklers for fire protection.

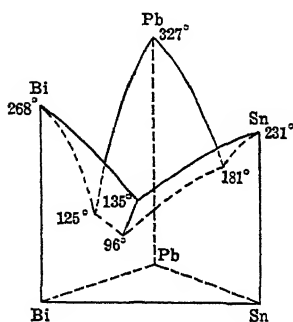


FIG. 98

In Fig. 98, the temperature is plotted vertically. The front plane gives the freezing-point curves of bismuth and tin with a eutectic at  $135^\circ$ ; the plane at the left of the back gives the freezing-point curves for bismuth and lead with a eutectic at  $125^\circ$ ; and the remaining plane for lead and tin gives a eutectic at  $181^\circ$ . These curves are connected by three surfaces which meet in a point giving a eutectic at  $96^\circ$ , where all three metals freeze out together. This is

the lowest possible melting temperature that can be obtained from any mixture of these three metals and the exact composition of this ternary alloy is found by projecting a vertical line down from this point until it hits the triangular base.

Some three-component systems may be represented with rectangular coordinates at various temperatures by space models of the type shown in Fig. 99a. The concentration of ammonium sulfate in per cent by weight is plotted along the  $X$  axis, the percentage of sodium sulfate is plotted along the  $Z$  axis, and temperature is plotted along the  $Y$  axis at right angles to the two concentration axes. The meaning of this space model is made apparent by the three graphs which accompany the model. The left side of the model is shown at  $c$ , where the concentration of ammonium sulfate is zero. The figure gives simply the

concentration-temperature graph for sodium sulfate in water. It shows the solubility curve of  $\text{Na}_2\text{SO}_4$  and of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and the freezing-point curve along which ice separates. The bottom of the model shown at *d* gives the concentration-temperature graph for

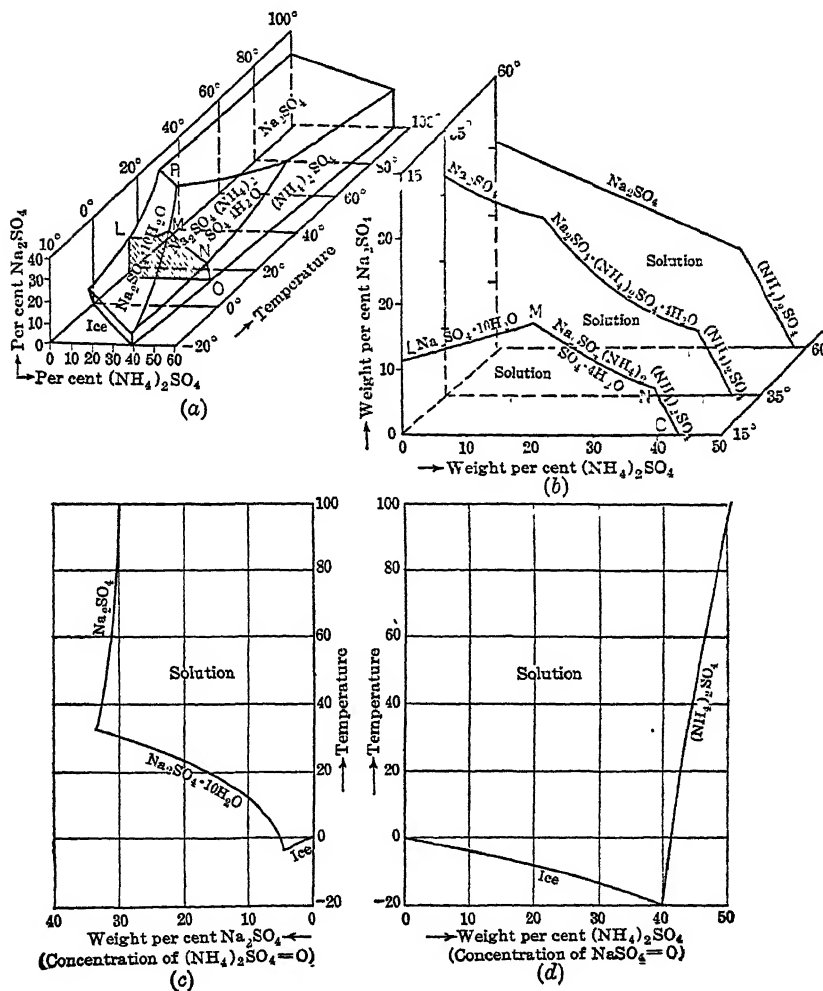


FIG. 99

ammonium sulfate, and the solubility curve and the freezing point are shown intersecting at the eutectic point. In Fig. 99*b* three isothermal planes are shown intersecting the space model at 15°, 35°, and 60°. The model is constructed by placing Figs. 99*c* and 99*d* at



right angles and spacing the isothermal concentration curves shown at  $b$  for the two salts at the proper intervals along the temperature axis. If desired, plaster of paris or other plastic material could be used to construct a space model along the curves given in these three dimensions.

The isothermal section at  $15^\circ$  is labeled  $L.M.N.O$  in Figs. 99*a* and *b*. The solubility of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  in pure water at  $15^\circ$  is 11 per cent by weight. As  $(\text{NH}_4)_2\text{SO}_4$  is added to the solution the solubility of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  increases along the line  $LM$ . When the solution contains 21 per cent  $(\text{NH}_4)_2\text{SO}_4$  the solubility of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is 16.5 per cent (expressed as per cent of  $\text{Na}_2\text{SO}_4$ ). When more ammonium sulfate is added, a double salt makes its appearance along  $MN$ , and the more ammonium sulfate is added the lower is the solubility of this double salt. The line  $NO$  represents the decrease in solubility of  $(\text{NH}_4)_2\text{SO}_4$  at  $15^\circ$  caused by the addition of  $\text{Na}_2\text{SO}_4$  to the solution. Similar curves are shown for  $35^\circ$  and  $60^\circ$ .

In the space model shown in Fig. 99*a* the pressure is fixed and the vapor is considered to be condensed. All the volume inside the space model refers to unsaturated salt solution. It is the only phase present and there are three degrees of freedom. Percentages of two components in the solution and temperature must be specified in order to define the system completely. ( $F = 3 - 1 + 1 = 3$ ). The various solid phases touching the model are specified on the model. For example, on top of the model there is  $\text{Na}_2\text{SO}_4$ , at the right there is  $(\text{NH}_4)_2\text{SO}_4$ , over the curved face is the double salt  $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  and in front of the model is ice. At these surfaces there are two phases (solution and a solid phase). Along the lines there are three phases, and at the points of intersection there are four phases. The degrees of freedom are respectively 2, 1, and 0. For example, at the point  $P$  there are  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  and solution; then  $F = 3 - 4 + 1 = 0$ .

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## PROBLEMS

1. Sketch a phase-rule diagram for thallium and mercury based on the following facts: mercury melts at  $-39^{\circ}$ ; the compound  $\text{Tl}_2\text{Hg}_3$  melts at  $15^{\circ}$ , thallium melts at  $303^{\circ}$ ; thallium lowers the freezing point of mercury down to a minimum of  $-60^{\circ}$  at a composition of 8 per cent thallium; the eutectic point for Tl and  $\text{Tl}_2\text{Hg}_3$  is  $0.4^{\circ}$  at a composition corresponding to 41 per cent thallium.

2. The following cooling curves have been found for the system antimony-cadmium.

Per cent cadmium by weight	0	20	37.5	47.5	50	58	70	93	100
First break in curve $^{\circ}\text{C}$ .	—	550	461	—	419	—	400	—	—
Continuing constant temp. $^{\circ}\text{C}$ .	630	410	410	410	410	439	295	295	321

Construct a phase diagram assuming that no other breaks than these actually occur in any cooling curve. Label the diagram completely and give the formula of any compound formed.

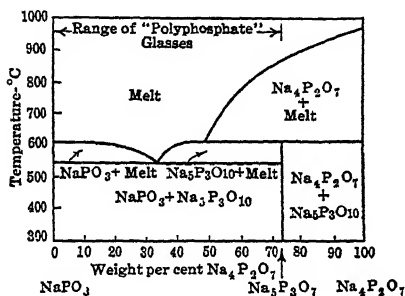


FIG. 100

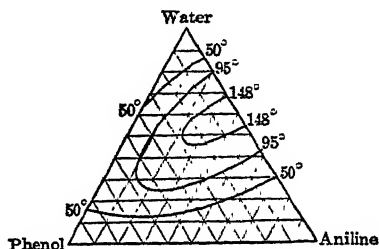


FIG. 101

3. Interpret the diagram of the mixed phosphates shown in Fig. 100 and state the number of degrees of freedom at a typical line, point, and area. State what will happen on cooling a typical concentration of the fused phosphate mixture.

4. Interpret the phase diagram shown in Fig. 101.

5. The following data are available for the system  $\text{Na}_2\text{SO}_4 - \text{Al}_2(\text{SO}_4)_3 - \text{H}_2\text{O}$  at  $42^{\circ}$ . Draw the phase diagram on triangular coordinate paper and draw in some appropriate tie lines.

Liquid Phase	
Wt. % $\text{Na}_2\text{SO}_4$	Wt. % $\text{Al}_2(\text{SO}_4)_3$
33.20	0
32.00	1.52
31.79	1.87
28.75	1.71
24.47	2.84
16.81	5.63
10.93	10.49
4.72	17.11
1.75	18.59
0	16.45

Composition of Solid Phase	
$\text{Na}_2\text{SO}_4$	
$\text{Na}_2\text{SO}_4$	
$\text{Na}_2\text{SO}_4$	
$\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$	
$\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$	
$\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$	
$\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$	
$\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$	
$\text{Al}_2(\text{SO}_4)_3$	
$\text{Al}_2(\text{SO}_4)_3$	

6. Referring to Fig. 90 choose two areas, two lines, and two points and state what components and what phases are present. State how many degrees of freedom there are at each of these areas, lines, and points.

7. Construct and interpret the phase diagram based on the following data where  $N_{\text{PbI}_2}$  is the mole fraction of lead iodide and  $t$  is the freezing point of the solution in degrees centigrade for the system KI — PbI<sub>2</sub>.

$N_{\text{PbI}_2}$	100	90	80	70	60	50	40	30	20	10	0
$t$	412	395	367	324	337	349	422	504	585	641	686°

8. Interpret the following vapor-pressure curve for mixtures of diethyl ether and magnesium bromide.

Moles (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O										
Moles MgBr <sub>2</sub>	1.73	1.51	1.18	1.00	0.99	0.90	0.85	0.82		
Vapor pressure (mm.)	3.87	3.92	3.91	3.92	1.39	1.30	1.30	1.26		

9. The following data are available for the system NiSO<sub>4</sub> — H<sub>2</sub>SO<sub>4</sub> — H<sub>2</sub>O at 25°. Sketch the phase diagram on triangular coordinate paper and draw appropriate tie lines.

<i>Liquid Phase</i>		<i>Composition of Solid Phase</i>
Wt. % NiSO <sub>4</sub>	Wt. % H <sub>2</sub> SO <sub>4</sub>	
28.13	0	NiSO <sub>4</sub> ·7H <sub>2</sub> O
27.34	1.79	"
27.16	3.86	"
26.15	4.92	NiSO <sub>4</sub> ·6H <sub>2</sub> O
22.26	7.93	"
15.64	19.34	"
10.56	44.68	"
9.65	48.46	NiSO <sub>4</sub> ·H <sub>2</sub> O
2.67	63.73	"
0.23	72.38	"
0.12	91.38	"
0.11	93.74	NiSO <sub>4</sub>
0.08	96.80	"

10. Interpret the phase diagram for the iron-carbon system given on page 609 of Vol. II of International Critical Tables.\*

11. Interpret the three-dimensional model representing the system aniline-sulfur dioxide, as worked out by Hill and shown in Fig. 102. (*J. Am. Chem. Soc.*, **53**, 2598 [1931].)

12. Interpret the phase diagrams for the polyiodides of cesium published by Briggs and Hubbard, *J. Phys. Chem.*, **45**, 821 (1941).

\* McGraw-Hill Book Co., New York, 1927.

13. The following are the data for the system methylcyclohexane-aniline-*n*-heptane at 1 atm. and 25°. Draw a triangular diagram for the system, including tie lines, and compute the exact composition of the first drop of the second liquid phase

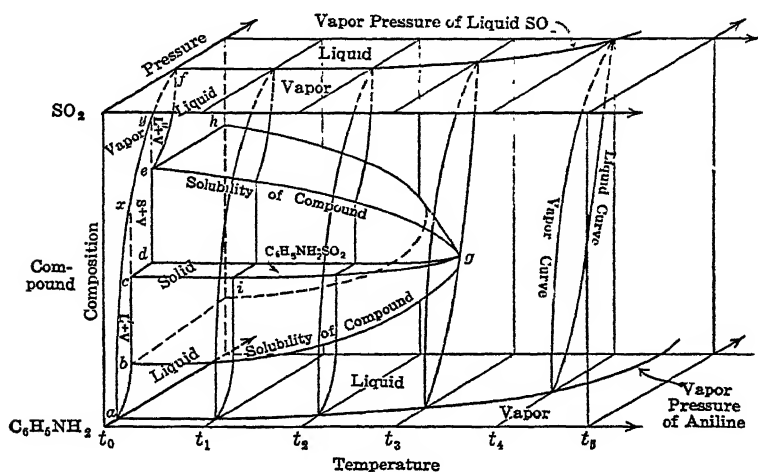


FIG. 102

which would separate if pure aniline were added to a 40 per cent solution of methylcyclohexane in *n*-heptane until separation occurred.

Hydrocarbon Layer		Aniline Layer	
Wt. %	Wt. %	Wt. %	Wt. %
Methylcyclohexane	<i>n</i> -Heptane	Methylcyclohexane	<i>n</i> -Heptane
0.0	92.0	0.0	6.2
9.2	83.0	0.8	6.0
18.6	73.4	2.7	5.3
33.8	57.6	4.6	4.5
46.0	45.0	7.4	3.6
59.7	30.7	9.2	2.8
73.6	16.0	13.1	1.4
83.3	5.4	15.6	0.6
88.1	0.0	16.9	0.0

## CHAPTER XIV

### CHEMICAL KINETICS

The aim of chemical kinetics is to predict the rates of chemical reactions and to describe the course of the reaction. It is a more difficult field than thermodynamics and the prediction of chemical equilibria, because the latter are concerned only with the initial and final states and not with time or with mechanisms, or with intermediate states. Science has not progressed as far in chemical kinetics, but the mere fact that the study of kinetics is a pioneer field adds interest to the subject. Many processes involve two or more reactions which are going on simultaneously in a very complicated manner. Impurities and traces of catalysts are likely to change the velocities, so that it is often difficult to obtain reproducible results. In fact it must be admitted that, in controlling the velocity of reactions for practical purposes, the art is still ahead of the science.

Most of the ionic reactions of inorganic chemistry take place so fast that their rates cannot be measured, but in many of the reactions of organic chemistry the study of chemical kinetics is particularly important. If two organic substances are mixed together there may be many different products which are all possible according to thermodynamics. Most of the reactions of organic chemistry are slow and the relative rates of competing reactions are often more important considerations than is the extent to which the reactions are completed at equilibrium. That material which is produced by the fastest reaction will predominate. By altering the concentrations and the temperature and by using specific catalysts, it is possible to bring about a desired reaction. If the desired reaction cannot be made much faster than all the other competing reactions, the yield will be low.

**Experimental Measurements of Reaction Rates.** The rate of a chemical reaction may be followed in many different ways. Samples may be removed at intervals, chilled rapidly, and analyzed by titration or other analytical methods. Again several bulbs of reacting material may be started out together; each is chilled quickly at different time intervals and analyzed. The chilling must be so rapid that the concentration does not change appreciably during the sampling process.

Physical means of analysis which do not disturb the system are convenient. If one of the reactants or products rotates the plane of polarized light its concentration may be determined during the course of the reaction with the help of a polarimeter. Again the concentration of one of the materials may be followed by measuring the absorption of light at a given wavelength and applying Beer's Law. Frequently this method is not practical because more than one colored material is present. The use of ultraviolet and infrared light makes possible wider applications of this method.

An increase in volume of a solution measured during the course of the reaction may be followed in a large thermometer bulb or a dilatometer. Again the volume of gas evolved by certain reactions in a liquid solution may be taken as a measure of the extent of the reaction. The volume  $V_0$  is measured at the beginning, and the volume  $V_x$  when the reaction has been completed. Measurements of volume  $V_t$  are taken at various times  $t$  during the reaction. Then  $V_x - V_0$  is a measure of the total amount of material which can react and  $V_x - V_t$  is the measure of the amount of material which still remains unreacted at time  $t$ . Then the fraction of the material remaining unreacted at time  $t$  is given by the expression  $(V_x - V_t)/(V_x - V_0)$ .

*Example 1.* When nitrogen pentoxide decomposes in carbon tetrachloride solution, oxygen gas is evolved. In one experiment 23.95 ml. of gas was evolved during one hour's time and after standing till no more gas was given off, the total volume of the gas was 34.75 ml. What fraction of nitrogen pentoxide remained undecomposed after one hour?

$$\text{Fraction undecomposed} = \frac{34.75 - 23.95}{34.75} = 0.311$$

Electrical conductivity of a solution or total pressure of a gas, are other physical properties which may be used in a similar manner to follow the rate of a chemical reaction. In complicated reactions, however, it is unwise to use total pressure as a measure of the extent of decomposition unless the measurements are accompanied by chemical or physical analyses which are specific for one or more of the reacting materials.

*Example 2.* In the gaseous reaction  $\text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_4 + \text{HBr}$ , the pressure increased from 200 mm. at the beginning to 390 mm. at the end. After 500 seconds the pressure was 300 mm. What fraction remained undecomposed? Assuming that the pressure should double to 400 mm. at the end, as indicated by the equation, half of the material would be left, i.e.,  $(400 - 300)/200 = 0.50$ . However, the fact that the final pressure was 10 mm. less than 400 mm. indicates that there is some complication involved and the calculation is not entirely safe. Obviously some other reaction in addition to the one written on paper is involved.

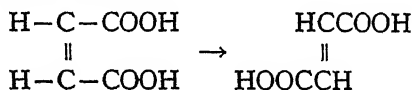
In gas reactions a flow method is sometimes used. The volume of the gases divided by the volume of the vessel in which the reaction takes place gives a measure of the time during which the gases are in the vessel. The vessel may be heated to a higher temperature or it may be filled with a catalyst. The gases issuing from the vessel are analyzed. It is difficult to get exact results by this method, but it is useful in many industrial processes.

*Example 3.* A volume of 1200 ml. of nitrogen pentoxide gas was passed through a heated tube 60 ml. in volume in 30 minutes. Approximately how long was each molecule exposed to this higher temperature? Time =  $60/(1200/30) = 1.5$  minute.

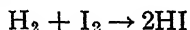
**Reaction Mechanisms.** In a *unimolecular reaction* only one molecule reacts at a time. It may break up into smaller parts as in the dissociation of bromine at high temperatures



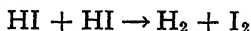
or it may merely undergo a rearrangement as when maleic acid is converted into fumaric by heating



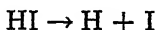
In a *bimolecular* reaction two molecules must come together before reaction can take place. They may be of different kinds as in the formation of hydriodic acid



or of the same kind as in the dissociation of hydriodic acid which occurs at a higher temperature

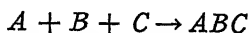


in the example just given one could write the reaction as a unimolecular reaction

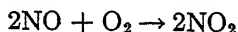


but the energy required to produce the free atoms of hydrogen and iodine is so great that reaction does not ordinarily go by this mechanism.

In a *termolecular* reaction three molecules combine as, for example, in the reaction



or in the oxidation of nitric oxide

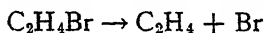
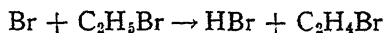
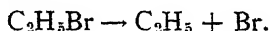


Termolecular reactions are rare, and reactions involving the simultaneous collision of more than three reactants are never found.

Most reactions are quite complex and really involve a series of steps, some fast and some slow, but each of these steps is usually itself a unimolecular or bimolecular reaction. For example, the thermal decomposition of ethyl bromide may be written simply as the unimolecular reaction



The stoichiometrical quantities are given correctly by the equation, but the reaction may involve a series of steps with atoms and fragments such as the following:



The overall reaction as written on paper usually has little significance in chemical kinetics. It is more important to learn by experiment how the rate of the reaction is influenced by the concentration of the reacting materials and thus to establish the *order* of the reaction as described in the following section.

**First-Order Reactions.** A *first-order reaction* is one in which the rate of reaction is found by experiment to be directly proportional to the concentration of the reacting substance. Obviously the amount of material which reacts depends on the amount that is present; and if the volume is kept constant the situation is described mathematically as follows:

$$-\frac{dc}{dt} = kc \quad [1]$$

where  $c$  is the concentration of material,  $k$  is a proportionality factor,  $t$  is the time, and  $-dc/dt$  is the rate at which the concentration decreases.

Integrating this simple differential equation,

$$-\ln c = kt + \text{constant}$$

$$-\log c = \left(\frac{k}{2.303}\right)t + \text{constant} \quad [2]$$

It is evident from this equation that in a first-order reaction a straight line is produced when the logarithm of the concentration is



plotted against time. The velocity constant  $k$  can be evaluated by multiplying the slope of the line by 2.303.

Integrating equation (1) between the limits, concentration  $c_1$  at time  $t_1$ , and  $c_2$  at a later time  $t_2$ ,

$$\begin{aligned} -\int_{c_1}^{c_2} \frac{dc}{c} &= k \int_{t_1}^{t_2} dt \\ -\ln c_2 - (-\ln c_1) &= k(t_2 - t_1) \\ k &= \frac{2.303}{t_2 - t_1} \log \frac{c_1}{c_2} \end{aligned} \quad [3]$$

This equation may be modified to give the following equation:

$$k = \frac{2.303}{t} \log \frac{c_0}{c} \quad [4]$$

where  $c_0$  is the concentration at the beginning of the reaction when the time is zero and  $c$  is the concentration after time  $t$  has elapsed.

This equation is often written in the exponential form

$$c = c_0 e^{-kt} \quad [5]$$

Still another modification is used, in which  $a$  is the initial quantity of material in a given volume,  $x$  is the amount reacting in time  $t$ , and  $a - x$  is the amount remaining after time  $t$ . Then

$$\frac{dx}{dt} = k(a - x) \quad [6]$$

and

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \quad [7]$$

The constant  $k$  is called the *specific reaction rate constant* or the *velocity constant*. It is a number per unit of time and may be expressed in reciprocal seconds (or in other units of time). When, for example,  $k$  has a value of  $0.001 \text{ sec.}^{-1}$  the material is decomposing at a rate of 0.1 per cent per second.

Reaction rates may be described by giving the numerical value of  $k$ , or sometimes by giving the *period of half-life*,  $t_{1/2}$ , i.e., the time necessary for half of a given quantity of material to decompose. It is meaningless to speak of the time necessary for all the material to decompose, because, theoretically, an infinite time is required. For a first-order reaction

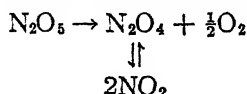
$$k = \frac{2.303}{t_{1/2}} \log \frac{1}{\frac{1}{2}} = \frac{0.693}{t_{1/2}}$$

The period of half-life in a first-order equation then is

$$t_{1/2} = \frac{0.693}{k} \quad [8]$$

The determination of the specific rate constant not only serves to describe the type of reaction mechanism but it makes possible a calculation of the amount of material which will react in a given time, or the time required for any specified portion of the material to react.

The calculation of first-order reaction rates may be illustrated with the decomposition of nitrogen pentoxide.\* Nitrogen pentoxide is a crystalline solid with a high sublimation pressure. It decomposes completely in the gas phase, or when dissolved in inert solvents, at a rate which is conveniently measured at room temperature. It is strictly first order, and its rate of decomposition has been checked in many different laboratories. The end products are oxygen and a mixture of  $N_2O_4$  and  $NO_2$ . The following equation represents the total reaction (but not the intermediate steps):



For every molecule of oxygen produced, two molecules of nitrogen pentoxide have decomposed.

When a solution of nitrogen pentoxide in carbon tetrachloride decomposes, the  $N_2O_4$  and  $NO_2$  remain in solution while the oxygen escapes and is measured in a gas buret. The reaction vessel is carefully thermostated and it is agitated to prevent supersaturation. The final volume of oxygen when the reaction is completed is a measure of the total amount of nitrogen pentoxide, and the difference between this final volume and the volume evolved at time  $t$  is a measure of the undecomposed nitrogen pentoxide still remaining.

Experimental data for the decomposition of nitrogen pentoxide at  $45^\circ$  are given in Table I, and plotted in the accompanying figures.

In Fig. 103a the concentration is plotted against time and the familiar mass-law relation is observed. The concentration decreases with time and approaches zero concentration very slowly.

In Fig. 103b the straight line produced by plotting the logarithm of the concentration against time shows that the reaction is first-order and follows strictly the relation given by equation (2).

\* Daniels and Johnston, *J. Am. Chem. Soc.*, **43**, 53 (1921); Eyring and Daniels, *ibid.*, **52**, 1472 (1930).

TABLE I  
DECOMPOSITION OF  $\text{N}_2\text{O}_5$  IN  $\text{CCl}_4$  SOLUTION AT  $45^\circ$

$t$ (seconds)	$c$ (moles/liter)	$\log c$	$-\frac{\Delta c}{\Delta t}$	Average $c$	$k$ equation (4) $\times 10^4$
0	2.33	0.367	.....	.....	.....
184	2.08	0.318	0.00136	2.20	6.32
319	1.91	0.281	0.00126	2.00	6.23
526	1.67	0.223	0.00116	1.79	6.22
867	1.36	0.133	0.00090	1.51	6.23
1198	1.11	0.045	0.00075	1.23	6.03
1877	0.72	1.857	0.00057	0.92	6.27
2315	0.55	1.740	0.00039	0.64	6.42
3144	0.34	1.531	0.00028	0.44	5.88

In Fig. 103*c* the values of  $-\Delta c/\Delta t$  obtained by taking increments of concentration and time between successive observations are plotted against the average concentration. The increments are sufficiently small so that the graph constitutes a confirmation of equation (1) and gives a straight line which runs into the origin. It shows that the rate of decrease in concentration with time is proportional to the concentration.

The value of the specific reaction rate as given in the last column of Table I ranges around 0.00062. The best value is 0.000622 as taken from the slope of the line in Fig. 103*b* and multiplied by 2.303, in agreement with equation (2). The slope of the straight line in Fig. 103*c* in agreement with equation (1) gives a value of  $k$  of 0.00062.

Sometimes it is inconvenient and unnecessary to determine so many points on the curve. If the reaction is first-order it will take twice as long for three-fourths of the material to decompose as it takes for half of it to decompose. This single criterion is sometimes useful.

After proving that the reaction is strictly first-order, the best value of the constant  $k$  can be determined from the slope of the straight line as in Fig. 103*b*, or by substituting two widely separated readings into formula (3). The best results are obtained when the first reading is chosen near the beginning of the experiment, as soon as the reaction vessel has reached the temperature of the thermostat, and the second one when the reaction is about two-thirds completed. In this way the errors of experimental measurement are reduced to a minimum. Two other independent readings over about the same range may be used as a check. It is not satisfactory to average all the constants obtained in successive time intervals using formula (3), for such a

procedure may cancel out all the intermediate readings and give a constant based only on the first and last readings. These readings are often the least accurate.\*

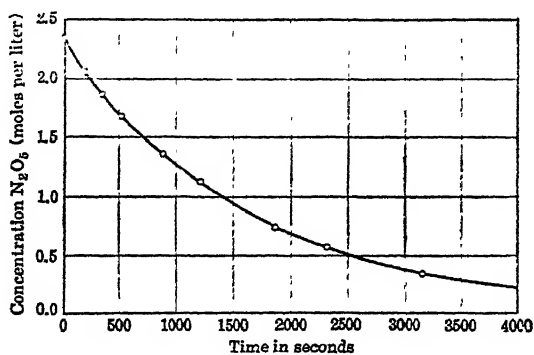


FIG. 103a

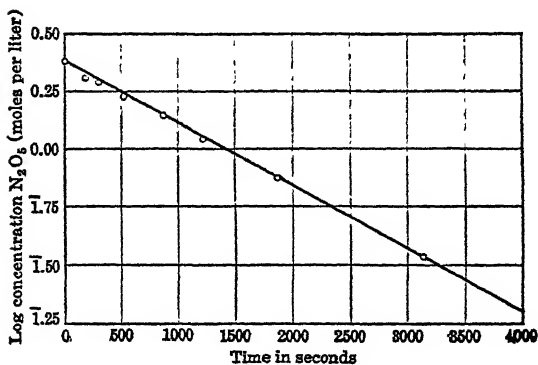


FIG. 103b

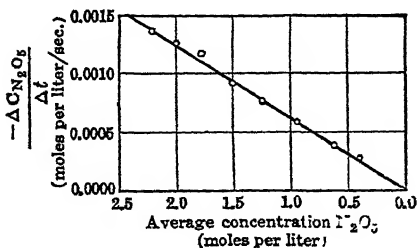


FIG. 103c

\* Mathematical methods for calculating rate constants are discussed critically by Roseveare, *J. Am. Chem. Soc.*, **53**, 1651 (1931); and by Reed and Theriault, *J. Phys. Chem.*, **35**, 673 (1931).

**Second-Order Reactions.** When the rate of a reaction as determined in the laboratory is proportional to the concentration of two reacting substances, the reaction is of the second order. Thus in the bimolecular reaction  $A + B \rightarrow AB$  if

$$-\frac{dc_A}{dt} = -\frac{dc_B}{dt} = kc_AC_B \quad [9]$$

the reaction is said to be of the second order.

If  $a$  and  $b$  represent the initial molar concentrations of the two reacting substances, and if  $x$  denotes the number of moles of  $A$  or  $B$  in each liter reacting in the interval of time  $t$ , then the velocity of the reaction is expressed by the equation

$$\frac{dx}{dt} = k(a-x)(b-x) \quad [10]$$

In the simplest case the two substances ( $A$  and  $B$ ) are present in equal concentrations and  $a = b$ . Under these conditions, the rate equation becomes,

$$\frac{dx}{dt} = k(a-x)^2 \quad [11]$$

Integrating equation (11)

$$\frac{1}{a-x} = kt + C \quad [12]$$

Evaluating the integration constant  $C$  by setting  $x = 0$  when  $t = 0$

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad [13]$$

If the reacting substances are not present in equivalent amounts, then equation (10) must be employed. On integrating\* and evaluating the integration constant, this becomes

$$kt = \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)}$$

or,

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad [14]$$

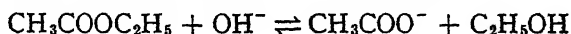
The graphical method for obtaining the best value of  $k$  is convenient and satisfactory unless the data are so accurate that the errors of

\* "Mathematical Preparation for Physical Chemistry," p. 189.

graphing are greater than the experimental error. Usually the experimental errors are greater. When  $\log [b(a-x)/a(b-x)]^*$  is plotted as ordinates against  $t$ , a straight line is obtained if the reaction is second-order, and  $k$  is then obtained by multiplying the slope of the line by  $2.303/(a-b)$ .

The value of  $k$  in a second-order reaction depends on the units in which the concentration is expressed, since the magnitude of the term  $(a-b)$  depends on the units used. For the sake of uniformity it is customary to express concentrations in moles per liter. The constant,  $k$  has the dimensions liters moles<sup>-1</sup> sec<sup>-1</sup>. In a first-order reaction the form of the equation is such that the units of concentration cancel out.

The hydrolysis of an ester by an alkali may be taken as an illustration of a second-order reaction. The reaction



has been studied by several investigators. Reactions of this type may be followed in a number of different ways. Solutions of ester and alkali are placed in separate flasks in a thermostat and then mixed.

TABLE II

## HYDROLYSIS OF ETHYL ACETATE AT 25°

$a$  = concentration of NaOH = 0.00980 mole per liter

$b$  = concentration of  $\text{CH}_3\text{COOC}_2\text{H}_5$  = 0.00486 mole per liter

Time seconds	$a - x$ moles/liter	$b - x$ moles/liter	$\log \frac{b(a-x)}{a(b-x)}$	$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$
0	0.00980	0.00486	.....	.....
178	0.00892	0.00398	0.0412	0.108
273	0.00864	0.00370	0.0640	0.109
531	0.00792	0.00297	0.1208	0.106
866	0.00724	0.00230	0.1936	0.104
1510	0.00645	0.00151	0.3266	0.101
1918	0.00603	0.00109	0.4390	0.106
2401	0.00574	0.00080	0.5518	0.107

At frequent intervals, a portion of the reaction mixture is removed, discharged into standard acid, and back-titrated with standard alkali. A final titration after the reaction is completed is necessary to determine the initial concentrations. The reaction may be followed also by measuring the change in the electrical conductance of the system

\* This is equivalent to  $\log [(a-x)/(b-x)] + \text{constant}$ .

or by measuring the slight increase in volume of the liquid as the reaction proceeds. The difference between the conductance or other physical property at a given time and at the completion of the reaction is a measure of the amount of material still to react, i.e., a measure of the concentration at that particular time.

Experimental data obtained by titration are recorded in the first three columns of Table II, and the specific rate constant  $k$  is given in the last column, as calculated by equation (14).

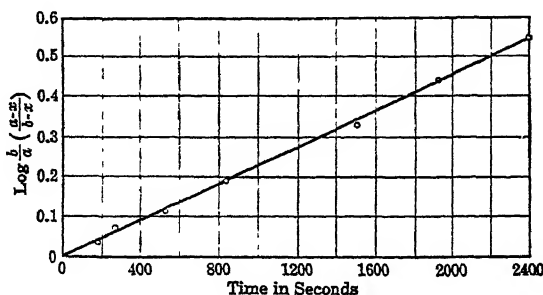


FIG. 104

The specific rate constant  $k$  can be determined easily and often with greater accuracy by a graphical method.

*Example 4.* Calculate  $k$  from the data of Table II, as shown in Fig. 104. The slope of the line is  $0.550/2400 = 0.000229$ .

$$k = \frac{2.303}{(a-b)t} \log \frac{b}{a} \frac{(a-x)}{(b-x)} = \frac{2.303}{0.00494} \times 0.000229 = 0.107$$

**Third-Order Reactions.** In a third-order reaction involving three substances  $A$ ,  $B$ , and  $C$

$$-\frac{dc_A}{dt} = -\frac{dc_B}{dt} = -\frac{dc_C}{dt} = kc_Ac_Bc_C$$

If the initial concentrations of the reacting substances are denoted by  $a$ ,  $b$ , and  $c$ , and if  $x$  denotes the concentration of each which is transformed in the interval of time  $t$ , the velocity of the reaction will be represented by the differential equation

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$$

If the substances are present in equivalent amounts,  $a = b = c$ , the corresponding equation is

$$\frac{dx}{dt} = k(a-x)^3$$

and

$$\frac{1}{2(a-x)^2} = kt + \text{constant} \quad [15]$$

The oxidation of nitric oxide to nitrogen dioxide is classed as a third-order reaction,\* and

$$\frac{dc_{\text{NO}_2}}{dt} = k c_{\text{NO}}^2 c_{\text{O}_2}$$

**Zero-Order Reactions.** There are reactions also in which the rate is unaffected by the concentration because it is determined by some other limiting factor such as the absorption of light in certain photochemical reactions or the rate of diffusion in certain surface reactions. Again the concentration of material may be kept constant automatically, as in a saturated solution. In such reactions the concentration of the substance  $A$  remains constant and is given by the formulas

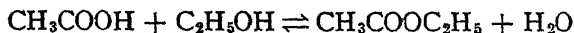
$$-\frac{dc_A}{dt} = k \quad [16]$$

$$c_A = -kt + \text{constant} \quad [17]$$

The constant  $k$  calculated in this way may include arbitrary constants corresponding to the fixed intensity of absorbed light or the concentration in a saturated solution or vapor.

**Complex Reactions.** The mathematical description of reaction rates thus far has been confined to a few standard types, but it must not be imagined that all reactions are amenable to simple mathematical treatment. The majority of reactions do not follow any of the three formulas, and are not simple first- or second- or third-order reactions. Frequently a reaction will follow one of these equations at first and then will gradually drift away from it. Among the various complications are (1) reverse reactions, (2) side reactions, (3) consecutive reactions. These disturbing causes will now be considered.

(1) *Reverse reactions.* In the chemical change represented by the equation



the speed of the direct reaction steadily diminishes, owing to the ever increasing effect of the reverse or counter reaction. Ultimately, when

\* Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).

Hasche and Patrick, *J. Am. Chem. Soc.*, **47**, 1207 (1925).

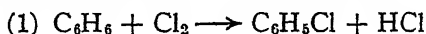
Smith, forthcoming publication.



about two-thirds of the acid and alcohol is decomposed, the velocities of the two reactions become equal and a condition of equilibrium results.

The simplest way to determine the specific reaction rate of the forward reaction is to measure the reaction rate at the beginning, before there is an opportunity to accumulate appreciable quantities of the products. As a matter of fact, reactions involving this counter effect are avoided if possible in theoretical studies in kinetics.

(2) *Side reactions.* When the same substances are capable of reacting in more than one way, with the formation of different products, the several reactions proceed side by side. Thus, benzene and chlorine may react in two ways, as shown by the equations

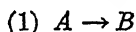


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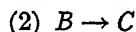


It is generally possible to regulate the conditions of temperature, concentration, solvent, or catalyst under which the substances react, so as to promote one reaction and retard the others.

(3) *Consecutive reactions.* By consecutive reactions, we understand those reactions in which the products of a certain initial chemical change undergo a second reaction. Many common chemical equations really represent the summation of a number of consecutive reactions. If the system *A* is transformed into the system *C*, through an intermediate system *B*, then there are the two reactions

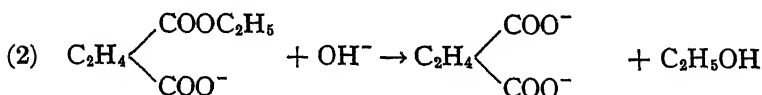
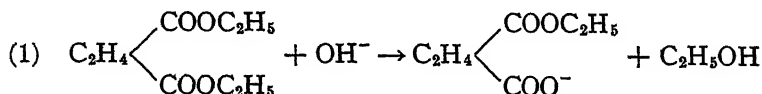


and



If reaction (1) has a very much greater velocity than reaction (2), then the measured velocity of the change from *A* to *C* is practically the same as that of the slower reaction (2).

The hydrolysis of ethyl succinate may be taken as an illustration of consecutive reactions. This reaction proceeds in two stages as follows:



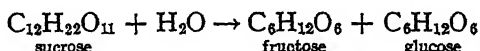
In this case, the product of the first reaction reacts with one of the original substances. It is less likely that one ethyl succinate molecule and two hydroxyl ions will collide and react simultaneously.

Consecutive reactions are very common. In fact the equations as ordinarily written give little idea of the intermediate steps, and yet one of these intermediate steps may be the slowest reaction, i.e., the rate-determining reaction. Kinetic measurements offer one of the best methods for studying intermediate steps in a reaction.

Simple reactions, like the oxidation of hydrocarbons to give carbon dioxide and water, really pass through a series of intermediate stages involving the production of peroxides, alcohols, ketones, and acids.

The decomposition of hydrogen peroxide represents another type of complex reaction. Hydrogen peroxide is fairly stable in the absence of catalysts but when it combines with a substance such as ferric chloride (probably to give ferric acid) the decomposition is rapid. Although the reaction involves two reacting substances, one of them, i.e., the ferric chloride, is released unchanged after the reaction. The concentration of the ferric chloride remains constant and equation (9) reduces to equation (1) since  $c_B$  is constant.

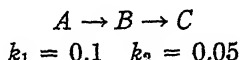
There are many cases in which the reaction mechanism is more complicated than appears from the simple rate equation. For example, the inversion of cane sugar in aqueous solution proceeds according to the following bimolecular equation when hydrogen ions are present:



The rate of the reaction is followed by measuring the rotation of polarized light. Although water and hydrogen ions play an active part in this reaction, the concentration does not appear to change, because the water is present in large excess. For example, in a 0.5 molal solution there are 111 molecules of water to every molecule of sugar, and when the sugar has completely reacted, the water will have been reduced by less than 1 per cent. The second-order equation reduces to the simple first-order equation since one of the reactants is essentially constant.

**Mathematical Analysis of Complex Reactions.** Perhaps the majority of chemical reactions involve consecutive reactions and the only hope of simplicity lies in having one of the reactions much slower than the rest. If all but one of the steps in the total overall reaction are immeasurably fast, the slow or rate-determining reaction is easily studied.

When two or more reactions are proceeding simultaneously at measurable rates the situation becomes complicated, as shown for example in the two first-order reactions



in which the specific reaction rates are 0.1 and 0.05 per hour, respectively. At the beginning of the reactions it is imagined that there is 1 mole of  $A$  and none of  $B$  or  $C$ . After a time  $t$ ,  $x$  moles of  $A$  have decomposed at the rate of 10 per cent per hour producing  $x$  moles of  $B$  and leaving  $1 - x$  moles of  $A$ . But  $B$  also decomposes, and does so at the rate of 5 per cent per hour. After time  $t$ ,  $y$  moles of  $C$  have been produced. The amount of  $B$  is the result of a balance between formation and decomposition and at any time  $t$  it is represented by  $x - y$ .

The decomposition rate of  $A$  is given by the equation

$$\frac{-d(1 - x)}{dt} = k_1(1 - x) \quad [18]$$

The rate of formation of  $C$  is given by the equation

$$\frac{dy}{dt} = k_2(x - y) \quad [19]$$

The amount of  $A$  at any time is obtained by integrating the first equation to give  $(1 - x) = e^{-0.1t}$ , and the amount of  $C$  is obtained by substituting this value of  $x$  into equation (19) and solving the differential equation to give  $y = 2(1 - e^{-0.05t}) - (1 - e^{-0.1t})$ . The amount of  $B$  at any time is merely the difference between  $x$  and  $y$ .

The amounts of  $A$ ,  $B$ , and  $C$  as calculated from these formulas are recorded at various times in Table III and Fig. 105.

If the course of the reaction were followed by analyzing for  $A$ , curve  $A$  would be obtained; if it were followed by measuring the quantity of the end product  $C$ , curve  $C$  would result; and finally if only the intermediate product  $B$  were determined the course of the reaction would rise to a maximum and then fall off as shown by curve  $B$ . The broken line  $D$  gives the rate at which the decomposition product of  $A$  would be formed in case it did not undergo further decomposition. The actual rate of production of  $C$  is seen to be quite complicated, and the existence of a slow induction period at the beginning of the reaction is evident.

This example is given in some detail because it illustrates a comparatively simple example of a complicated reaction. When the rate

TABLE III

CONSECUTIVE REACTIONS  $A \longrightarrow B \longrightarrow C$   
 $k = 0.1 \quad k = 0.05$

Amounts of A, B, and C at various times starting with 1 mole of A

Time $t$	Quantity A $(1 - x) = e^{-0.1t}$	$e^{-0.05t}$	Quantity C $y$	Quantity B $x - y$
0	.1	1.	0	0
10	0.368	0.606	0.156	0.476
20	0.135	0.368	0.399	0.466
30	0.0498	0.223	0.604	0.346
40	0.0183	0.135	0.748	0.234
50	0.00674	0.0821	0.842	0.151
60	0.00248	0.0498	0.903	0.095

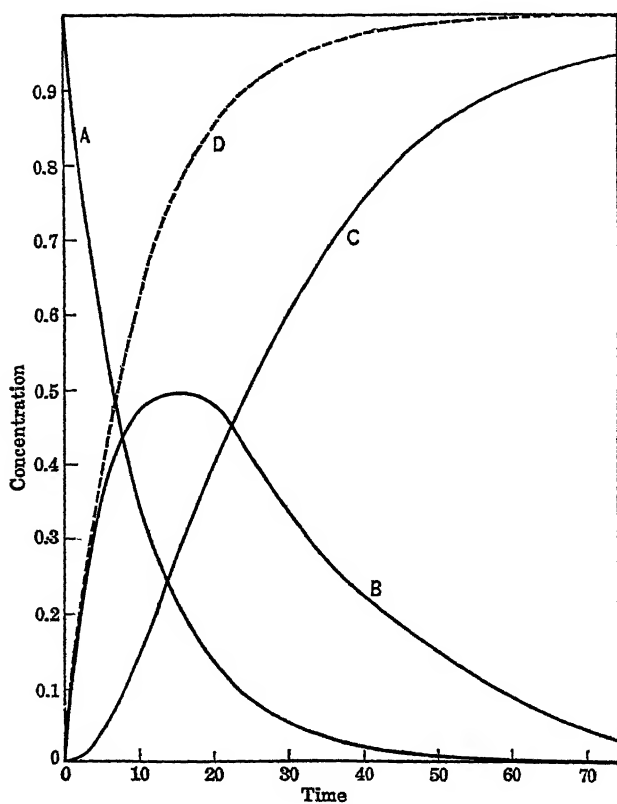


FIG. 105

of each of the steps is known the overall reaction rate can be built up as shown, provided that it is possible or practical to carry out the operations of integration. In laboratory practice the situation is usually much more difficult for the overall reaction is known and the problem is to determine the rates of the intermediate steps. Not only is it difficult to solve the resulting differential equations but also it is even more difficult to be sure that the set of reactions thus determined is the only set that will be in accord with the observed facts.

Reverse reactions as well as consecutive reactions may be treated mathematically if the equilibrium constant is known, making allowance for the reverse reaction. Starting with  $a$  moles of acetic acid and  $a$  moles of alcohol in the reaction  $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$ , the rate of the forward reaction is given by the expression

$$\frac{dx}{dt} = k_1(a - x)^2 \quad [20]$$

where  $x$  represents the amount of acid and alcohol reacting, or the amount of ester and water formed at the time  $t$ , and  $k_1$  is the specific reaction rate of the forward reaction.

The rate of the reverse reaction is given by the expression

$$- \frac{dx}{dt} = k_2 x^2 \quad [21]$$

where  $k_2$  is the specific reaction rate at which the concentration of the products, ester and water, decrease.

The actually observed rate, including both forward and reverse reactions, is

$$\frac{dx}{dt} = k_1(a - x)^2 - k_2 x^2 \quad [22]$$

But from the definition of the equilibrium constant,

$$K = \frac{k_1}{k_2}$$

or

$$k_2 = \frac{k_1}{K} \quad [23]$$

and

$$\frac{dx}{dt} = k_1(a - x)^2 - \frac{k_1}{K} x^2 \quad [24]$$

In the reaction between acetic acid and ethyl alcohol, at room temperature,  $K$  has the value 4.0, and equation (24) may be integrated and solved for  $k_1$ .

There are many other kinetic expressions which combine competing, consecutive, or reverse reactions each of which may involve either a first-order or a second-order equation.\* Many of the more complicated ones are difficult or impossible to integrate. Often valuable information can be obtained from the rate equation without integration and it is easy to understand why there are sometimes induction periods and why complex reactions may approach a first or second order or a fractional exponent for a while during the course of the reaction.

*Example 5.* Set up a rate expression for the following reactions, (1) and (2), which go on simultaneously.



$$(3) \quad \frac{dc_A}{dt} = -k_1c_A + k_1'c_Bc_C - k_2c_Ac_B$$

$$(4) \quad \frac{dc_D}{dt} = k_2c_Ac_B$$

$$(5) \quad \frac{dc_C}{dt} = k_1c_A - k_1'c_Bc_C$$

$$(6) \quad \frac{dc_B}{dt} = k_1c_A - k_1'c_Bc_C - k_2c_Ac_B$$

It may be assumed that after a short induction period,  $B$  is consumed by the reaction to give  $D$  as fast as it is produced from  $A$ , and that a steady state exists in which

$$\frac{dc_B}{dt} = 0$$

(7) Then under this condition

$$c_B = \frac{k_1c_A}{k_1'c_C + k_2c_A}$$

\* For a fuller treatment the student is referred to Moelwynn Hughes, "Physical Chemistry," Oxford University Press, 1941, Appendix 9, and to Sherwood and Reed, "Applied Mathematics in Chemical Engineering," McGraw-Hill Book Co., New York, 1939.

and

$$(8) \quad \frac{dc_D}{dt} = k_2 c_A c_B = \frac{k_1 k_2 c_A^2}{k'_1 c_C + k_2 c_A}$$

and since 2 moles of  $A$  disappear for each mole of  $D$  produced

$$(9) \quad -\frac{dc_A}{dt} = \frac{2k_1 k_2 c_A^2}{k'_1 c_C + k_2 c_A}$$

The rate of this reaction depends on the concentration of both  $A$  and  $C$ . When  $k_2 c_A$  is small compared to  $k'_1 c_C$  the rate of change of the concentration of  $A$  depends on  $c_A^2$  and the reaction is second order with respect to the reacting substance  $A$ ; when  $k_2 c_A$  is large compared to  $k'_1 c_C$  the rate depends on  $c_A$  and the reaction is first order with respect to  $A$ .

In actual practice the exponent of  $c_A$  may shift gradually from first order through mixed orders to second order with respect to  $A$  as the reaction proceeds.

**Determination of the Order of a Reaction.** Simple examples have been given of clean-cut first-, second-, third-, and zero-order equations but as shown in the preceding section it must not be supposed that all observed chemical reactions fit these types. The order of a reaction is determined by the exponents of concentration terms from which the rate of the reaction is determined. For example, in the reaction  $A + B \rightarrow X$ , the rate expression is

$$\frac{dc_X}{dt} = k c_A^m c_B^n \quad [25]$$

The rate of production of  $X$  depends on the concentration  $c$  of each of the materials taking part in the reaction each raised to an exponent which is determined empirically by experiment. Sometimes the exponents such as  $m$  and  $n$  are whole numbers, 1, 2, 3, etc., representing the number of moles of the material taking part stoichiometrically in the reaction. An example was given in equation (9). It is just as likely, however, that the experimental data will show that the rate of formation of  $X$  or the disappearance of  $A$  is given by an expression with fractional exponents such, for example, as

$$-\frac{dc_A}{dt} = k c_A^{1.3} c_B^1 \quad [26]$$

This situation emphasizes the fact that frequently there is little relation between the stoichiometrical reaction as written on paper and the order of the reaction as determined in the laboratory. In fact, most chemical reactions are complex, involving two or more different reactions or reaction steps going on simultaneously, although each of

these intermediate reactions is likely to be a unimolecular or bimolecular reaction.

The sum of all the exponents involved in the rate equation is taken as the order of the reaction. Thus, in equation (9) it is second order, in equation (15) it is third order and in equation (26) it is 2.3 order. There are several different ways in which the order of a reaction may be determined.

*Substitution into formulas.* If a reaction is of first, second, third, or zero order, a constant value of  $k$  will be obtained throughout the course of the reaction when the data are substituted into the proper formula. If none of the formulas can be made to fit, the reaction is complicated and probably two or more reactions are going on simultaneously.

*Graphing.* The order may sometimes be determined by plotting different functions of the concentration  $c$  against the time. If a straight line is obtained when  $\log c$  is plotted against time the reaction is first order as shown in equation (2).

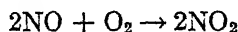
In the special case where all the reactants have the same initial concentration, the reaction is second order if a straight line is obtained when  $1/c$  is plotted against time, as shown in equation (12), and third order if a straight line is obtained when  $1/c^2$  is plotted against time as shown in equation (15).

In a zero-order reaction a straight line is obtained when  $c$  is plotted against time as is evident from equation (17).

*Half-life periods.* In a first-order reaction the period of half-life (or in fact the time required for any given fraction to react) is independent of the initial concentration as shown in equation (8).

In a second-order reaction in which  $a = b$  the time required for a given fraction to react is inversely proportional to the initial concentration, and  $t_{1/2} = 1/ka$ .

*Variation in ratio of reactants.* When different molecules are involved, the course of the reaction may be studied by altering the ratio of the reacting materials. For example, the oxidation of nitric oxide



is accelerated more by increasing the concentration of nitric oxide than by increasing the concentration of oxygen. This fact is in accord with the equation

$$\frac{dc_{\text{NO}_2}}{dt} = kc_{\text{NO}}^2 \times c_{\text{O}_2}$$

Much information may be gained in a complex reaction by increas-



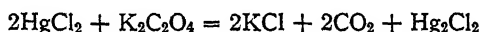
ing greatly the concentration of the reactants, one at a time, and observing the change in the reaction rate over a short period of time (for example, a period in which the change in composition is not over 10 per cent). Since

$$\frac{dx}{dt} = kc_A^m \cdot c_B^n \cdot c_C^j$$

where  $A$ ,  $B$ , and  $C$  represent the different molecules reacting and  $m$ ,  $n$ ,  $j$  are the corresponding exponents in the rate equation, it is seen that  $m$  can be evaluated by doubling  $c_A$ , keeping  $c_B$  and  $c_C$  constant, and determining  $\Delta x/\Delta t$  experimentally in the two cases. Thus, for short intervals where  $\left(\frac{\Delta x}{\Delta t}\right)_{2c_A}$  is the observed rate when the concentration of  $A$  is doubled, giving  $2c_A$  instead of  $c_A$

$$\left(\frac{\Delta x}{\Delta t}\right)_{2c_A} / \left(\frac{\Delta x}{\Delta t}\right)_{c_A} = \frac{k2^m c_A^m c_B^n c_C^j}{k c_A^m c_B^n c_C^j} = 2^m$$

*Example 6.* The chemical equation for the reaction between potassium oxalate and mercuric chloride is:



The weight of  $\text{Hg}_2\text{Cl}_2$  precipitated from different solutions in a given time, at  $100^\circ$ , was as follows:

	$\text{HgCl}_2$ (moles per liter)	$\text{K}_2\text{C}_2\text{O}_4$ (moles per liter)	Time (min.)	Moles of $\text{Hg}_2\text{Cl}_2$ precipitated
(1)	0.0836	0.404	65	0.0068
(2)	0.0836	0.202	120	0.0031
(3)	0.0418	0.404	60	0.0032

Write the differential equation for the reaction rate, evaluating the exponents of the concentrations.

$$\frac{dx}{dt} = kc_{\text{HgCl}_2}^m c_{\text{K}_2\text{C}_2\text{O}_4}^n$$

From (1) and (2)

$$\left(\frac{\Delta x}{\Delta t}\right)_{2\text{K}_2\text{C}_2\text{O}_4} / \left(\frac{\Delta x}{\Delta t}\right)_{c_{\text{K}_2\text{C}_2\text{O}_4}} = \frac{0.0068/65}{0.0031/120} = 4 = \frac{k(c_{\text{HgCl}_2})^m (2c_{\text{K}_2\text{C}_2\text{O}_4})^n}{k(c_{\text{HgCl}_2})^m (c_{\text{K}_2\text{C}_2\text{O}_4})^n} = 2^n$$

Since  $2^n = 4$ ,  $n = 2$ . From (1) and (3)

$$\left(\frac{\Delta x}{\Delta t}\right)_{2\text{HgCl}_2} / \left(\frac{\Delta x}{\Delta t}\right)_{c_{\text{HgCl}_2}} = \frac{0.0068/65}{0.0032/60} = 2 = \frac{k(2c_{\text{HgCl}_2})^m (c_{\text{K}_2\text{C}_2\text{O}_4})^n}{k(c_{\text{HgCl}_2})^m (c_{\text{K}_2\text{C}_2\text{O}_4})^n} = 2^m$$

Since  $2^m = 2$ ,  $m = 1$ . Then,

$$\frac{dx}{dt} = k c_{\text{HgCl}_2}^1 c_{\text{K}_2\text{C}_2\text{O}_4}^2$$

It will be noted that the rate depends on the square of the potassium oxalate concentration although the stoichiometric equation indicates that only one molecule is involved. Again the reaction as written is bimolecular with respect to mercuric chloride, but first order with respect to the concentration of mercuric chloride. These differences show that the reaction is complex and that the equation as written does not represent the full course of the reaction with its rate-determining intermediate steps.

*Addition of excess of reactant.* Often a complex reaction may be simplified and studied by adding a large excess of one or more of the reactants so that they do not undergo appreciable change during the reaction. If all but one of the reacting substances is present in large excess a variation of this one reactant permits a direct determination of the exponent to which the concentration of the reactant is raised in the rate equation.

**Influence of Temperature.** It has long been known as an empirical fact that many reactions approximately double or treble their velocity for a  $10^\circ$  rise.

A more quantitative relation, proposed by Arrhenius, is given in the following equation

$$k = s e^{-\Delta H_a / RT} \quad [27]$$

where  $s$  is a constant and  $\Delta H_a$  is another constant, which is now interpreted as the heat of activation as explained later on page 372. Setting in logarithmic form

$$\log k = \frac{-\Delta H_a}{2.303R} \frac{1}{T} + \text{constant} \quad [28]$$

Differentiating

$$\frac{d \ln k}{dT} = \frac{\Delta H_a}{RT^2} \quad [29]$$

and integrating between limits

$$\log \frac{k_2}{k_1} = \frac{\Delta H_a}{2.303R} \left( \frac{T_2 - T_1}{T_2 T_1} \right) \quad [30]$$

It will be noted that these equations are similar to those for equilibrium constants studied on page 297. According to equation (28), a straight line is produced when the logarithm of the specific reaction

rate is plotted against the reciprocal of the absolute temperature. The specific decomposition rates of gaseous nitrogen pentoxide\* at different

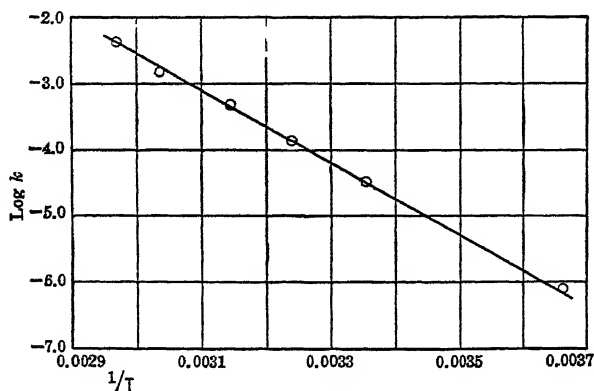


FIG. 106

temperatures are given in the third column of Table IV, and they are shown graphically in Fig. 106.

TABLE IV  
DECOMPOSITION OF NITROGEN PENTOXIDE AT DIFFERENT TEMPERATURES

$t^\circ$	$1/T$	$k_{\text{obs.}} \times 10^5$	$\log k$	$k_{\text{calc}} \times 10^5$	Half-Life
65	0.002959	487	-2.313	477	2.38 min.
55	0.003048	150	-2.824	155	7.72 min.
45	0.003145	49.8	-3.303	47.2	21.8 min.
35	0.003247	13.5	-3.871	13.2	85.9 min.
25	0.003357	3.46	-4.471	(3.46) <sup>1</sup>	5.71 hours
0	0.003663	0.0787	-6.104	0.0733	10.2 days

<sup>1</sup> The value of  $k_{\text{obs}}$  at  $25^\circ$  was used for calculating  $k_{\text{calc}}$ .

The slope of the line in Fig. 106 is  $-5400$ , and  $\Delta H_a$  has the value of  $24,700$ . Equation (28) becomes

$$\log k = -\frac{24,700}{2.303 \times 1.987} \frac{1}{T} + 13.638 \quad [31]$$

and equation (27)

$$k = 4.3 \times 10^{13} e^{\frac{-24,700}{1.987T}}$$

Using this formula, the calculated specific reaction rates are given in

\* Daniels and Johnston, *J. Am. Chem. Soc.*, **43**, 53 (1921).

the fifth column of the table. The periods of half-life, calculated from the data in the third column, are given in the last column.

The marked influence of temperature on reaction rates is clearly brought out in this table. Extrapolated values based on equation (31) are shown in Table V. It should be emphasized that the range between reactions which are too slow to measure and those which are too fast to measure is comparatively narrow. Ordinary laboratory measurements have usually been limited to the range between minutes and months.

TABLE V  
EXTRAPOLATED VALUES OF HALF-LIFE

$t^\circ$	Half-Life	$t^\circ$	Half-Life
300	0.000039 sec.	25	5.7 hours
200	0.0039	0	11 days
150	0.088	-25	3 years
125	0.56	-50	830 years
100	4.6	-75	940,000 years
75	51.	-100	8.4 billion years

A few other first-order gas reactions together with the Arrhenius constants are given in Table VI.

TABLE VI  
FIRST-ORDER GAS PHASE REACTIONS

Decomposing Substance	Specific Reaction Rate	Decomposing Substance	Specific Reaction Rate (seconds <sup>-1</sup> )
(1) $\text{N}_2\text{O}_5$	$k = 4.3 \times 10^{13} e^{-24,700/RT}$	(5) $\text{C}_2\text{H}_5\text{Br}$	$k = 3.8 \times 10^{14} e^{-54,800/RT}$
(2) $\text{SiH}_4$	$k = 2 \times 10^{13} e^{-51,700/RT}$	(6) $\text{ClCO}_2\text{C}_2\text{H}_5$	$k = 5.5 \times 10^{-10} e^{-29,400/RT}$
(3) $\text{Pb}(\text{C}_2\text{H}_5)_4$	$k = 1.2 \times 10^{12} e^{-36,900/RT}$	(7) $\text{CH}_3\text{N}_3$	$k = 3 \times 10^{15} e^{-43,500/RT}$
(4) $\text{N}_2\text{O}$	$k = 4.2 \times 10^9 e^{-53,000/RT}$	(8) Stilbene	$k = 6 \times 10^{12} e^{-42,800/RT}$

1. Daniels and Johnston, *J. Am. Chem. Soc.*, **43**, 53 (1921).
2. Hogness, Wilson, and Johnson, *J. Am. Chem. Soc.*, **58**, 108 (1936).
3. Leermakers, *J. Am. Chem. Soc.*, **55**, 4508 (1933).
4. Nagasako and Volmer, *Z. physik. Chem.*, **10B**, 414 (1930).
5. Vernon and Daniels, *J. Am. Chem. Soc.*, **55**, 922 (1933).
6. Choppin, Frediani, and Kirby, *J. Am. Chem. Soc.*, **61**, 3176 (1939).
7. Leermakers, *J. Am. Chem. Soc.*, **55**, 2719 (1933).
8. Isomerization of *cis*-stilbene, Kistiakowsky and Smith, *J. Am. Chem. Soc.*, **56**, 638 (1934).

**Kinetic Theory of Gases.** Information concerning the distribution of energy among molecules and the frequency of collisions may be obtained from the kinetic theory of gases. This in turn is valuable in the study of reaction rates.

The unordered motion of colloid particles has been directly observed under the microscope, and we have every reason to believe that the motions of molecules in a gas are similar. A series of collisions in the right direction may give to a molecule an abnormally high velocity, and on the other hand a head-on collision may completely stop a molecule for a brief interval of time. Since the velocities are determined by chance, and since a large number of molecules is involved

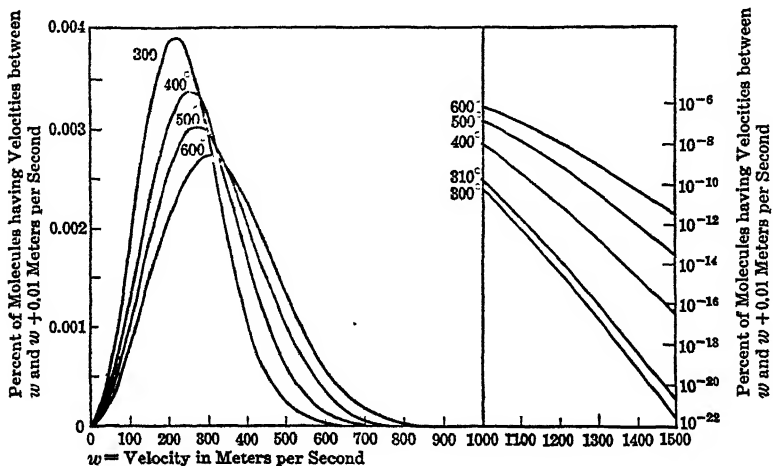


FIG. 107

in any measurement, the laws of probability may be applied with exactness.

The distribution of velocities is known as the Maxwell distribution law. It is illustrated in Fig. 107 for gaseous nitrogen pentoxide, which has a molecular weight of 108. It is seen that there is a most probable velocity which varies with the temperature and that there are very few molecules with very high or very low velocities.

It is only the molecules which possess extremely high velocities that are of any interest in chemical reactions. For example, in nitrogen pentoxide an energy of 24,700 cal. per mole, equivalent to a velocity of nearly 1400 m. per second, is required for decomposition.

In other words, those molecules with velocities of about 1400 m. per second or more have sufficient energy to undergo chemical reaction. The relative number of these "activated" molecules is exceedingly small at room temperature and hence the reaction is slow. As shown by the exaggerated scale at the right the number of these rapidly moving molecules is greatly increased by an increase in temperature.

The mathematical statement of the distribution of velocities is

$$\frac{dn}{n_t} = 4\pi \left( \frac{M}{2\pi RT} \right)^{3/2} e^{-Mc^2/2RT} c^2 dc \quad [32]$$

where  $M$  is the molecular weight,  $c$  is the probable velocity of the molecule and  $dn/n_t$  is the fraction of the molecules having velocities between  $c$  and  $c + dc$ ,\*  $n_t$  being the total number of molecules.

Introducing  $E$ , the energy expressed in calories per mole,

$$E = \frac{1}{2}Mc^2$$

$$dE = Mc \, dc$$

$$\frac{dn}{n} = \frac{2}{\sqrt{\pi}} \left( \frac{1}{RT} \right)^{3/2} e^{-E/RT} E^{1/2} dE \quad [33]$$

This gives the fraction of the molecules having energies between  $E$  and  $E + dE$ .

Of particular interest in physical chemistry is the number of molecules  $n'$  having energies greater than some fixed value  $E$  (expressed in calories per mole). For many purposes it is sufficient to define the term  $n'/n_t$  by the approximate expression

$$\frac{n'}{n_t} = e^{-E/RT} \quad [34]$$

A more exact expression is obtained by integrating equation (33) by parts between the limits  $E$  and  $\infty$ .†

*Example 7.* Calculate at 25° and at 35° the fraction of nitrogen pentoxide molecules having a kinetic energy equal to or greater than 24,700 cal. per mole,

\* An excellent derivation may be found in Glasstone, "Textbook of Physical Chemistry," D Van Nostrand Co., New York, 1940, p. 258.

† The integration is

$$\begin{aligned} \frac{n'}{n_t} &= \int_E^\infty \frac{2}{\sqrt{\pi}} \left( \frac{1}{RT} \right)^{3/2} e^{-E/RT} E^{1/2} dE \\ &= \frac{2}{\sqrt{\pi}} \left( \frac{E}{RT} \right)^{1/2} e^{-E/RT} \left\{ 1 + \frac{RT}{2E} - \left( \frac{RT}{2E} \right)^2 + \dots \right\} \end{aligned}$$

In practical applications  $E$  is large compared to  $RT$ , and so the only term of importance in the brackets is the first, or

$$\frac{n'}{n_t} = \frac{2}{\sqrt{\pi}} \left( \frac{E}{RT} \right)^{1/2} e^{-E/RT}$$

and calculate the effect of a  $10^\circ$  rise in temperature on this fraction

$$\text{at } 25^\circ \quad \frac{n'}{n_t} = \frac{2}{\sqrt{\pi}} e^{-E/RT} \sqrt{\frac{E}{RT}} = \frac{2}{\sqrt{\pi}} e^{-24,700 / (1.987 \times 298.1)} \sqrt{\frac{24,700}{1.987 \times 298.1}} \\ = 5.69 \times 10^{-18}$$

$$\text{at } 35^\circ \quad \frac{n'}{n_t} = \frac{2}{\sqrt{\pi}} e^{-24,700 / (1.987 \times 308.1)} \sqrt{\frac{24,700}{1.987 \times 308.1}} = 2.17 \times 10^{-17}$$

$$\frac{n' / n_{35^\circ}}{n' / n_{25^\circ}} = \frac{2.17 \times 10^{-17}}{5.69 \times 10^{-18}} = 3.81$$

This increase of 381 per cent in the fraction of activated molecules is in close agreement with the increase in the reaction rates at  $35^\circ$  and  $25^\circ$  as given in Table IV,

$$\frac{13.2 \times 10^5}{3.46 \times 10^3} = 3.82$$

indicating that the major increase in the reaction rate is due to an increase in the fraction of activated molecules. It should be emphasized that the total kinetic energy of the gas,  $3RT/2$ , increases only 3.3 per cent when the temperature is raised from 298.1 to 308.1. Most of this energy, however, is too low to do anything chemically. Only kinetic energy of 24,700 cal. per mole or greater is effective in bringing about this reaction and this high-intensity energy is increased greatly by a  $10^\circ$  rise, as shown.

**Molecular Collisions in Gases.** Four quantities of use in chemical kinetics may be calculated from the kinetic theory of gases introduced in Chapter II. They are (1) the number of molecules striking a surface, (2) the number of collisions per second between molecules in a gas, (3) the molecular diameters, and (4) the distance a molecule travels before colliding with another molecule.

(1) *Number of molecules striking a surface.* If  $n$  molecules are contained in a cube 1 cm. on an edge, it may be assumed that one-sixth of them are moving toward one wall. The root-mean-square velocity is  $u$  centimeters per second, and the number of molecules hitting the wall in a second will be equal to one-sixth of the number which are within a distance of  $u$  centimeters from it. Even if one of these molecules is prevented from hitting the wall by colliding with another molecule, the second molecule will be deflected back so that the number of hits is the same. If there are  $n$  molecules in the 1-cm. cube, the number hitting one wall (1 sq. cm.) is  $\frac{1}{6}nu$  ( $1^2$ ). A closer analysis which allows for unequal speeds and collisions at oblique angles gives  $1/\sqrt{6}\pi$  or 0.230 instead of  $1/6$ . Then

$$\text{Collisions per square centimeter of wall per second} = 0.230nu \quad [35]$$

It was shown on page 35 that

$$u = \sqrt{\frac{3RT}{M}} \quad [36]$$

Since  $u$  is expressed in centimeters per second,  $R$  must be expressed in ergs per degree to keep both in c.g.s. units.

(2) *Frequency of collisions.* A rough idea of the number of collisions between molecules may be obtained from the following considerations. If the diameter of a molecule is  $\sigma$  and two molecules are just touching, the distance separating their centers is also  $\sigma$ . Considering molecules to be points, each molecule can collide with all other molecules which come within the distance  $\sigma$  from its center. A molecule moving with a velocity of  $u$  centimeters per second will sweep out during a second a cylindrical space  $u$  centimeters long with an *effective* cross section  $\pi\sigma^2$ . The cylindrical space may be zigzag in shape on account of deflections suffered during collisions. If there are  $n$  molecules per cubic centimeter, this molecule will collide with  $(\pi u \sigma^2)n$  other molecules. But each of the  $n$  molecules will sweep out this effective volume and undergo the same number of collisions. The total number of molecules undergoing collisions is therefore  $(\pi u \sigma^2 n)n$ . Certain approximations are involved in this derivation, and when corrections are made for the distribution of velocities and other factors, the number of molecules colliding is given more exactly by the expression

$$\frac{4}{3}\sqrt{3\pi} u \sigma^2 n^2 \quad \text{or} \quad 4.09 u \sigma^2 n^2$$

The number of collisions is one-half the number of molecules colliding because two molecules are necessary for a collision. The number of collisions  $z$  per second per milliliter is given by the equation

$$z = 2.05 u \sigma^2 n^2 \quad [37]$$

Substituting for  $u$  its equivalent given in (36), combining and rounding off numbers, the following approximate equation is obtained:

$$z = 3.54 \sigma^2 n^2 \sqrt{\frac{RT}{M}} \quad [38]$$

(3) *Molecular diameters.* All the quantities necessary for calculating the frequency of collisions are readily obtainable, except the molecular diameter  $\sigma$ . This quantity can be calculated from the viscosity measurements, similar to those described for liquids on page 167. A few values are given in Table VII.



TABLE VII  
 MOLECULAR DIAMETERS ( $\sigma$ )

Gas	$\sigma$	Gas	$\sigma$
Helium	$2.18 \times 10^{-8}$ cm.	Hydrochloric acid	$2.86 \times 10^{-8}$ cm.
Argon	3.36	Hydrobromic acid	3.16
Chlorine	4.96	Hydriodic acid	3.50
Bromine	3.42	Carbon dioxide	4.18
Iodine	3.96	Hydrogen	2.47
Oxygen	3.39	Nitrogen pentoxide	8.53
Nitrogen	3.50		

Many of the diameters calculated from viscosity measurements are in close agreement with the diameters as calculated from x-ray measurements on crystals, and there is good evidence that the diameters of most molecules are of the order of  $10^{-8}$  cm. or a few Ångström units. In fact, when no data are available, it may be assumed for the purpose of estimating the number of collisions that the molecular diameter is  $10^{-8}$  cm. In certain phenomena involving radiation, however, molecules appear to have effective diameters which are much larger.

(4) *Mean free path.* If a molecule travels  $u$  centimeters in a second and collides with  $\pi u \sigma^2 n$  molecules per second as shown before, the average distance between encounters  $l$ , called the mean free path, is given by the equation

$$l = \frac{u}{\pi u \sigma^2 n} = \frac{1}{\pi \sigma^2 n}$$

Closer analysis shows that

$$l = \frac{1}{\sqrt{2} \pi \sigma^2 n} \quad [39]$$

A knowledge of the mean free path is useful in calculations involving collisions in chemical reactions and rates of diffusion of gases.

In all these formulas, (35), (36), (37), (38), and (39), the velocities  $u$  are given as the root-mean-square velocities. The average velocities and the most probable velocities vary slightly from these values.

*Example 8.* Nitrogen is contained in a vessel at 1 atm. pressure at  $25^\circ$ . Calculate: (a) the number of collisions on the walls per second per square centimeter; (b) the number of collisions between molecules per second per milliliter; (c) the mean free path.

It is necessary first to calculate the number of molecules  $n$  per milliliter and

the velocity of the molecules,  $u$ ,

$$n = 6.02 \times \frac{10^{23}}{\left(22,400 \times \frac{298.1}{273.1}\right)} = 2.46 \times 10^{19}$$

$$u = \sqrt{\frac{3RT}{M}} = \left(\frac{3 \times 8.315 \times 10^7 \times 298.1}{28}\right)^{1/2} = \sqrt{26.56 \times 10^8} \\ = 5.15 \times 10^4 \text{ cm. sec}^{-1}.$$

$$(a) \ 0.230nu = 0.230 \times 2.50 \times 10^{19} \times 5.15 \times 10^4 \\ = 2.92 \times 10^{23} \text{ collisions cm.}^{-2} \text{ sec.}^{-1}.$$

$$(b) \ 2.05u\sigma^2n^2 = 2.05 \times 5.15 \times 10^4 \times (3.50 \times 10^{-8})^2 \times (2.46 \times 10^{19})^2 \\ = 7.8 \times 10^{28} \text{ collisions between molecules ml.}^{-1} \text{ sec.}^{-1}.$$

$$(c) \ l = \frac{1}{\sqrt{2\pi\sigma^2n}} = \frac{1}{1.41 \times 3.14 \times (3.50 \times 10^{-8})^2 \times 2.50 \times 10^{19}} \\ = 7.5 \times 10^{-6} \text{ cm.} = \text{the mean free path.}$$

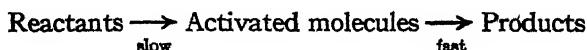
**Activation of Molecules.** According to present theories, it is necessary for molecules to become activated before they can react. If all molecules were equally reactive, it would be difficult to account for the very existence of slow reactions. Since the number of collisions per second is enormous, it might be expected that all reactions would be instantaneous. Ionic reactions, such as neutralizations and precipitations, are in fact immeasurably fast, but the ionic state may be regarded as an activated state.

Chemical equilibria and thermodynamics involve only the initial and final states and they are not concerned with the mechanisms of the reaction nor with the intermediate steps. In chemical kinetics, however, we are interested in the reaction steps which lead to the final products and we try to apply our thermodynamical calculations not to the whole reaction but to the activation process.

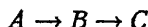
Thus in the overall reaction



we are concerned with  $\Delta H$ , which is equal to  $H_{\text{products}} - H_{\text{reactants}}$ , but in chemical kinetics the same reaction is written



or



and we are concerned with the slow or rate-determining step for which

$$\Delta H_a = H_{\text{activated molecules}} - H_{\text{reactants}}$$

For the reverse reaction  $C \rightarrow B$ ,  $\Delta H'_a = H_{\text{activated molecules}} - H_{\text{products}}$

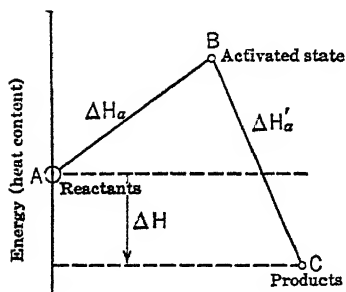


FIG. 108

The relation between the heat of reaction and the heats of activation is given in Fig. 108.

The initial molecules  $A$  require the absorption of a definite amount of heat  $\Delta H_a$  in order to put them in an activated state  $B$  from which they can rearrange to give the products  $C$ . In order to reverse the reaction the molecules  $C$  must be supplied with the heat of activation

$\Delta H'_a$  and therefore in passing from the activated state  $B$ , to  $C$ , an amount of heat equal to  $\Delta H'_a$  is evolved. The heat of reaction measured in a calorimeter at constant pressure is equal to the difference between the heat of activation in the two directions.

$$\Delta H = \Delta H_a - \Delta H'_a \quad [40]$$

Usually the heat evolved in the step  $BC$  is greater than the heat absorbed in the step  $AB$  and the overall reaction in going from  $A$  to  $C$  is an evolution of heat. If  $\Delta H_a$  happens to be greater than  $\Delta H'_a$  the reaction is endothermic.

It will be remembered that if the reaction is carried out at constant volume instead of constant pressure the heat of reaction is  $\Delta E$  rather than  $\Delta H$ . The two are practically the same in solutions, where there is but little change in volume, and even in gaseous reactions involving a change in volume the difference is usually small in comparison with the values of  $\Delta H$ .

The energy required for the activated state is the chief factor in determining the speed of the reaction. It was shown that the greater the energy required for activation the fewer are the molecules possessing this energy; and hence the slower is the reaction at a given temperature. The heat of reaction,  $\Delta H$ , is of no significance for calculating reaction rates. As Hinshelwood has suggested, there is no more connection between the heat of reaction and the energy of activation than there is between the difference in levels of two valleys and the height of a mountain pass which separates them.

One very useful generalization can be made, however. In endothermic reactions, the energy required for activation must be at least

as great as the endothermic heat of reaction. This is equivalent to saying that in going from a lower to a higher valley the route must go over an elevation at least as high as the upper valley. Often it is difficult to calculate the energy of activation, but, if the reaction is endothermic, the heat of reaction may be used as a *minimum* value.

*Example 9.* The heat of combustion of a carbohydrate is 112,000 cal. per mole of carbon. To effect the reverse reaction, namely, the combination of carbon dioxide and water to form a carbohydrate what is the minimum activation energy required?

Since this reverse reaction is endothermic by 112,000 cal., an activation energy of at least 112,000 cal. must be supplied. It is quite possible that more than 112,000 cal. will be necessary.

The heat of activation,  $\Delta H_a$ , cannot be measured calorimetrically because the activated molecules have only a brief existence. It is determined indirectly by plotting  $\log k$  against  $1/T$  and multiplying the slope by  $2.303R$  just as heat of reaction is determined by plotting  $\log K$  against  $1/T$ , where  $K$  is the equilibrium constant (page 296). In this way the heat of activation was found on page 364 to be 24,700 cal. per mole for the decomposition of nitrogen pentoxide.

*Example 10.* Combining equations (29) and (40), show that the Arrhenius equation can be used to derive the known relation between equilibrium constants and heat of reaction.

$$\frac{d \ln k}{dT} = \frac{\Delta H_a}{RT^2} \quad \text{and} \quad \frac{d \ln k'}{dT} = \frac{\Delta H'_a}{RT^2}$$

where  $k$  and  $\Delta H_a$  refer to the forward reaction and  $k'$  and  $\Delta H'_a$  refer to the reverse reaction.

Subtracting

$$\frac{d(\ln k - \ln k')}{dT} = \frac{\Delta H_a - \Delta H'_a}{RT^2}$$

$\Delta H = \Delta H_a - \Delta H'_a$ , and from page 274  $k/k' = K$ . Then

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

This relation was proved by thermodynamics on page 295, thus lending support to the validity of the Arrhenius equation.

**The Arrhenius Equation.** The considerations just discussed apply to free energy as well as to heat content, and

$$\Delta F = \Delta F_a - \Delta F'_a \quad [41]$$

It is now worth while to examine more fully the Arrhenius equation

$$k = s e^{-\Delta H_a/RT}$$

and to interpret the constants in terms of physical chemical concepts. Since  $\Delta H_a$  and  $RT$  are expressed in the same units, usually calories,  $e^{-\Delta H_a/RT}$  is dimensionless. Then  $s$  has the same dimensions as  $k$ , and for first-order reactions, involves a number per second.

The rate of the overall reaction depends on the concentration of the activated molecules and this concentration may be calculated with the help of thermodynamical relations. There is an equilibrium between reacting and activated molecules and

$$K_a = \frac{c_{\text{activated}}}{c_{\text{reactant}}}$$

It will be remembered (pages 133 and 289) that

$$\Delta F = \Delta H - T \Delta S$$

and that

$$\Delta F^0 = -RT \ln K$$

Then

$$K_a = e^{-\Delta F_a^0/RT} = e^{\Delta S_a/R} e^{-\Delta H_a/RT} \quad [42]$$

There are complications involved in calculating the concentration of the activated molecules from this equilibrium constant and the concentration of the reactants. The more complete rate equation is derived in part in the appendix on page 666. It is

$$k = \frac{RT}{Nh} e^{\Delta S_a/R} e^{-\Delta H_a/RT} \quad [43]$$

This is the fundamental equation of Eyring's theory of the "activated complex." For a complete interpretation the literature must be consulted.\*

This equation constitutes the proof, promised earlier, that the constant  $\Delta H_a$  in the Arrhenius equation is the *heat of activation*. Moreover, it is evident that the factor  $s$  in the Arrhenius equation, known as the frequency factor, has the following significance:

$$s = \frac{RT}{Nh} e^{\Delta S_a/R} \quad [44]$$

At ordinary temperatures the term  $RT/Nh$  is about  $(8.3 \times 10^7 \times 300)/(6.0 \times 10^{23} \times 6.5 \times 10^{-27})$  or  $10^{13}$ . This is the same order of magni-

\* Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, 1941.

tude as the frequency in the infrared spectrum (page 577) which is due to the natural vibration period of atoms within the molecule. The term  $e^{\Delta S_a/R}$  is an entropy term and for unimolecular reactions it may often be neglected particularly in gas reactions, because the activated complex is so much like the original reactants that the entropy change is very small. In some reactions, however, particularly in certain rearrangements and in bimolecular reactions, the entropy of activation may become fairly large and thus the frequency factor may become important in determining the reaction rate. In a series of related compounds the influence of structure on the reaction rate is sometimes a matter of changes produced in the entropy of activation. It must be remembered that these activated molecules or the activated complex have only a transitory existence and that it will probably never be possible to isolate them and make measurements on them. The value of  $\Delta S_a$  must be determined by indirect methods.

In many bimolecular reactions the frequency factor  $s$  turns out to be approximately equal to the number of molecules colliding, per unit volume and time, when at unit concentration. As a first approximation in such cases it may be supposed that the rate of reaction is determined by the rate at which *activated* molecules collide and give the products of the bimolecular reaction. On this hypothesis it is proportional to the number of molecules colliding multiplied by  $e^{-\Delta H_a/RT}$ , which is approximately equal to the fraction of molecules in the activated state. But there are many bimolecular reactions, particularly in solution, in which the reaction goes much more slowly than predicted by this formula. It has been customary to assume that a certain orientation at the time of collision, a type of lock-and-key effect, is necessary for complete reaction. The more exact statistical development giving  $(RT/Nh)e^{\Delta S_a/R}$  for the frequency factor leads to terms which are approximately equivalent to the product of the collision frequency and the orientation factor.

*Example 11.* In the bimolecular decomposition of gaseous hydriodic acid the heat of activation has been found by equation (30) to be 45,600 cal. Then at 393.7° from the last equation on page 367 using  $\Delta H_a$  for  $E$

$$e^{-\Delta H_a/RT} = e^{-45,600/(1.987 \times 666.8)} = 1.1 \times 10^{-15}$$

$$\frac{n'}{n} = \frac{2}{\sqrt{\pi}} e^{-\Delta H_a/RT} \sqrt{\frac{\Delta H_a}{RT}} = 7.3 \times 10^{-15}$$

If the concentration of hydriodic acid is 1 mole per liter, the number of

molecules colliding per milliliter is given by the expression

$$2z = 2 \times 3.54 \sigma^2 n^2 \sqrt{\frac{RT}{M}} = 2 \times 3.54 \times (3.5 \times 10^{-8})^2 \times \left( \frac{6.02 \times 10^{23}}{1000} \right)^2 \\ \times \sqrt{\frac{8.3 \times 10^7 \times 666.8}{127.9}} = 6.6 \times 10^{31}$$

Expressed in terms of moles colliding per second per liter

$$2z = 6.6 \times 10^{31} \times \frac{1000}{6.02 \times 10^{23}} = 1.1 \times 10^{11}$$

and substituting  $2z$  for the frequency factor in the Arrhenius equation at  $393.7^\circ$

$$k = s e^{-\Delta H_a/RT} = 1.1 \times 10^{11} \times 7.3 \times 10^{-15} = 8.0 \times 10^{-4}$$

The experimentally determined value is  $2.6 \times 10^{-4}$  mole<sup>-1</sup> liter. This fair agreement shows that there is no large orientation effect in this simple reaction.

**The Prediction of Reaction Rates.** The Arrhenius equation is found to fit the rate measurements on a surprisingly large number of different reactions at various temperatures. If the heat of activation is known from experimental measurements or if it can be estimated from theoretical considerations (page 654) it is possible to predict the reaction rate constant at any temperature provided that an approximate value can be assigned to the frequency factor. On account of the exponential character of the equation, it is more important in calculating the rate constant  $k$  to know the heat of activation accurately than it is to know the frequency factor with precision.

From what has been said in the preceding section, it is evident that for many unimolecular gas reactions the entropy of activation is small and the following relation holds approximately

$$k = 10^{13} e^{-\Delta H_a/RT} \quad [45]$$

In a critical survey\* of twenty-eight of the best examples of unimolecular gas phase reactions reported in the literature from 1936–41, the value of  $s$  in the Arrhenius equation was found to be between  $10^{12}$  and  $10^{14}$  in 60 per cent of the reactions and below  $10^{12}$  in only 4 per cent.

On the basis of these facts the chart of **Fig. 109** is useful in predicting reaction rates for many gas phase unimolecular decompositions.

The values of  $k$  in sec<sup>-1</sup> on the slanting lines are recorded at the right. It is a simple matter to obtain a rough estimate of  $k$  by graphical

\*Symposium, "Activation Energies," American Chemical Society, September, 1941.

interpolation. The situation is simplified by the fact that very rapid or very slow reactions are of no practical concern, the ordinary time of observation of the course of a reaction being not less than a few seconds nor more than a few months. The values of  $k$  falling within this time range are roughly from  $10^{-1}$  to  $10^{-7}$ .

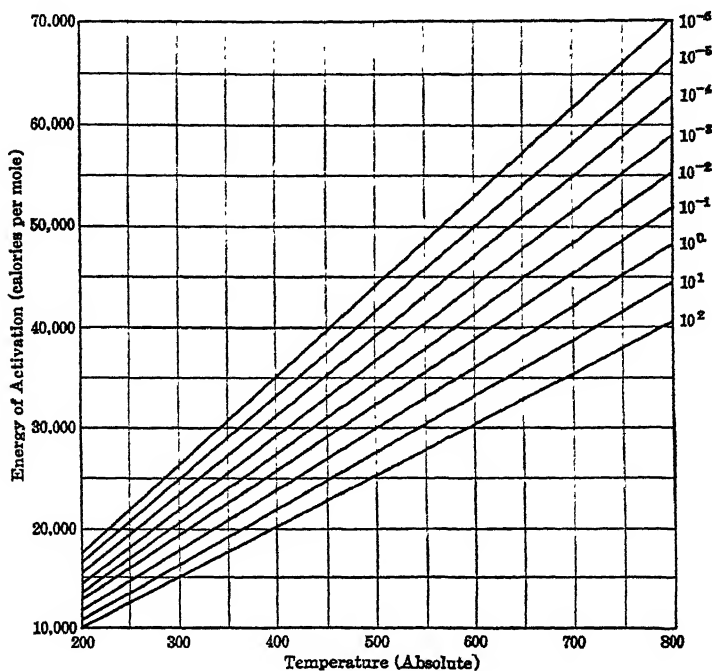


FIG. 109

If the energy of activation for a first-order reaction is 25,000 cal. per mole and the temperature is 300° K. (a little over room temperature),  $k$  has a value of  $10^{-5}$ , assuming that  $s$  has a value of  $10^{12}$ . When  $k$  is  $10^{-5}$  the period of half-life is about 19 hours. These data fit the case of nitrogen pentoxide fairly well.

Again, the energy of activation for the first-order decomposition of ethyl bromide is about 55,000 cal. per mole, and it is evident that the temperature must be above 650° K. to give appreciable decomposition. As another illustration it may be concluded that at 500° K. one is concerned in unimolecular reactions only with those reactions that have values of  $\Delta H_a$  between 25,000 and 45,000 cal. per mole. With larger values of  $\Delta H_a$  the reaction is too slow to measure; with smaller values it is too fast.

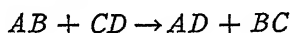


The chart may be used as a rough estimate in many reactions, but large errors are more likely to be made if it is used for unimolecular reactions in solutions. In bimolecular reactions it was seen that part of the frequency factor may be interpreted as the number of collisions. These depend on molecular weights and other factors but when they are expressed in moles per liter they have a value ranging around  $10^{10}$ . In bimolecular reactions then the expression

$$k = 10^{11} e^{-\Delta H_a/RT}$$

offers a possible but still more unsatisfactory means for predicting reaction rates. The entropy of activation or the orientation factor are likely to cause large departures from this estimate.

The prediction of activation energies from known physical chemical constants is unsatisfactory. One approach is indicated on page 654. There are a few empirical guides for calculating the activation energy in simple reactions\* among which may be cited the rule that in a four-atom reaction of the type



the heat of activation is equal to 28 per cent of the sum of the heats required to dissociate the two bonds  $AB$  and  $CD$ .

**Catalysis.** The velocity of a chemical reaction frequently is accelerated by the presence of a foreign substance which remains unchanged when the reaction is complete. For example, cane sugar is inverted very slowly by pure water alone, but when a trace of acid is added, the rate of inversion is greatly increased. A substance which accelerates a chemical reaction and is not consumed by it is termed a *catalyst*, and the process is known as *catalysis*.

A catalyst is powerless to change the position of equilibrium; it simply hastens the rate of attainment of equilibrium. The catalyst accelerates the reverse reaction to the same extent as the forward reaction so that their ratio, the equilibrium constant, is unaffected.

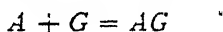
Sometimes the catalyst may *appear* to change the equilibrium but in such cases large quantities of the catalyst are usually required and the material not only accelerates the reaction but it also changes the activities or effective concentrations of the reacting materials. Changing the solvent, for example, may accelerate a reaction, and it may also change the equilibrium, but the two effects are entirely independent. The catalytic effect is not responsible for the equilibrium shift.

The function of the catalyst is to bring about the desired reaction with a smaller heat of activation. A lower heat of activation gives

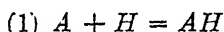
\* Hirschfelder, *J. Chem. Phys.*, **9**, 645 (1941).

a more rapid reaction because more molecules have the necessary amount of energy to react. Referring to Fig. 108, it will be seen that the finding of a catalyst is analogous to finding a lower route than the one represented by *B*, in passing from *A* to *C* and from *C* to *A*. The high energy requirement is avoided by some by-pass. Usually the by-passing consists in forming a new compound with less energy consumption and then decomposing this intermediate compound in such a way as to regenerate the catalyst. In this way the catalyst is used over and over again.

Thus if a reaction represented by the equation



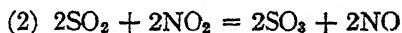
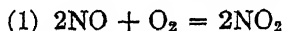
takes place very slowly under ordinary conditions, it is possible to accelerate its velocity by the addition of an appropriate catalyst *H*. Then



The catalytic action of nitrogen dioxide in the oxidation of sulfur dioxide offers a good example. The rate of the reaction represented by the equation



is very slow. The accelerating action of nitric oxide on the reaction may be represented in the following simplified manner:



Numerous examples in support of the intermediate compound theory of catalysis are found in the realm of organic chemistry. Probably the most familiar is the preparation of ether from alcohol using sulfuric acid as the catalyst. That an intermediate compound is actually formed in this reaction was first proved by Williamson, who detected the presence of ethyl sulfuric acid in the reaction mixture. The catalytic action of aluminum chloride in the well-known Friedel-Crafts synthesis of organic compounds has been shown to be due to the formation of an addition compound.

It must be emphasized that the conditions for catalysis are rather specific. If the intermediate compound is too stable, no further decomposition is possible. It must have just the right degree of stability.

Sometimes one of the products of reaction functions as a catalyst. Such a substance is called an *auto-catalyst*. Normally, of course, the reaction rate decreases continually, but in auto-catalytic reactions the rate increases to a maximum and then decreases.

**Contact Catalysis.** The phenomenon of adsorption has been described, and it was suggested that in many cases the surface of a solid may be regarded as a checkerboard of atoms on which molecules from the gas phase, or from solution, become attached. The adsorbed layer is then limited to a thickness of one molecule. There may be further condensation of easily liquefiable gases in the minute capillaries of substances like charcoal and silica gel, but this phenomenon is not ordinarily involved in catalysis.

When molecules are adsorbed at a surface the energy content is altered and there is opportunity for forming new products. Adsorption does not necessarily produce catalytic reactions, but catalytic reactions at surfaces generally involve adsorption. Apparently some atoms at the surface are in better position to bring about reaction than others. Moreover, the exact spacing between atoms in the lattice of the catalyst is important, and this distance can be altered by changing the method of preparation and adding extra substances.

The rate of a reaction catalyzed by a surface depends to a large extent on the fraction of the surface which is covered with adsorbed gas. When the surface is nearly bare the pressure of the gas determines the extent of adsorption, and this in turn determines the speed of the reaction. Since the reaction rate is proportional to the concentration of the gas, the reaction follows the first-order equation. When the surface remains practically saturated, on the other hand, the pressure of the gas has no influence on the reaction rate and the reaction is of the zero order. When ammonia is decomposed on a tungsten filament, for example, the rate of decomposition is independent of the pressure, over a wide range of pressure.

When the surface is partly covered, the reaction rate is proportional to  $p^n$  where  $p$  is the pressure and  $n$  is some fractional number which is determined empirically by experiment.

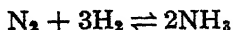
The activity of a catalyst is altered appreciably by extremely minute amounts of foreign substances. Foreign substances which tend to inhibit catalytic activity are known as *poisons*; substances which tend to enhance the activity are known as *promoters*. It is easy to see how a small number of molecules can react permanently with the few atoms at the surface to destroy the catalytic properties. For example, in the manufacture of sulfuric acid by the contact process, the presence of a very minute amount of arsenic completely destroys the catalytic

activity of the platinum catalyst by forming platinum arsenide at the surface. Certain metals and metallic oxides act as promoters in some cases by rendering the catalyst less susceptible to poisoning, but in many cases they act by increasing the interfaces at which loose adsorption compounds are formed, having just the right degree of stability to produce a rapid catalytic reaction. In the Haber process for the synthesis of ammonia with an iron catalyst, for example, the addition of a trace of certain metals such as vanadium produces a large increase in catalytic activity.

The catalytic activity of the walls of the containing vessel is a factor in many gaseous reactions. The thermal decomposition of organic materials frequently occurs on the walls. In such cases the temperature coefficient is usually small because the slowest process is the diffusion of the products away from the walls and a diffusion process is subject only to the simple laws of the kinetic theory of gases. A  $10^{\circ}$  rise at about  $300^{\circ}$  K. increases the diffusion rate only about 3 per cent, whereas a chemical reaction is normally increased about 300 per cent, as already explained. If the slowest step is the adsorption process, the temperature coefficient may be high, however, because such an adsorption is a type of chemical reaction. A wall effect may be distinguished from a homogeneous gas reaction by (1) the temperature coefficient, (2) increasing the area greatly, as by adding powdered glass to a glass vessel, (3) changing the nature of the vessel walls. Quartz may be used instead of glass, for example, or the walls may be coated. The reaction between bromine and ethylene is a wall effect, as shown by the fact that the reaction is stopped when the glass walls are covered with paraffin.

**Some Applications of Catalysis.** Only a few of the many applications of catalysis in the realm of industrial chemistry can be mentioned here.

*The Haber process for ammonia.* By a careful study of the conditions governing the equilibrium represented by the equation



and by the employment of proper catalytic agents, Haber succeeded in producing ammonia on a commercial scale by means of this reaction. The synthesis of ammonia is now one of the large chemical industries of the world. At  $1000^{\circ}$ , ammonia may be regarded as completely dissociated, while at  $550^{\circ}$ , under atmospheric pressure, only about 0.08 per cent of ammonia is formed. However, the formation of ammonia at this temperature would be altogether too slow, except

for the addition of a catalyst. Pure iron and special alloys of iron are effective catalysts. A practical catalyst not only must be efficient but also it must be stable and not too easily poisoned by traces of impurities.

In accordance with the principle of Le Chatelier, the equilibrium is shifted in the direction of the smaller volume, i.e., in the direction of the ammonia. Thus at  $550^{\circ}$  under a pressure of 200 atm. nearly 12 per cent of ammonia is formed. Despite the fact that this percentage is small, ammonia can be removed by ammonium nitrate as ammonia of crystallization or by other means. Fresh portions of hydrogen and nitrogen are then introduced into the reaction chamber, thus rendering the process continuous.

*Hydrogenation processes.* Toward the latter part of the nineteenth century, Sabatier and Senderens discovered that reduced nickel will bring about the combination of hydrogen with ethylene, or other unsaturated compounds. In this method of hydrogenation, the vapor of the substance to be reduced is mixed with hydrogen and passed over a catalyst, which is maintained at a temperature ranging from  $150^{\circ}$  to  $300^{\circ}$ . The process is rapid; furthermore, it requires a minimum amount of attention. The yields are relatively high, provided proper care is taken to maintain the temperature within the prescribed limits necessary to minimize the formation of secondary products.

Great care must be taken in the preparation of the catalyst since the success of the method is largely dependent upon the condition of the metal. The catalyst is susceptible to various poisons, particularly chlorine, sulfur, arsenic, and phosphorus, and their compounds.

Nickel catalysts and metallic oxide catalysts are used extensively for hydrogenating various liquids and dissolved substances with hydrogen under pressure.\* One of the most important industrial applications of the hydrogenation process is in the conversion of unsaturated aliphatic acids, such as oleic acid, into saturated acids, such as stearic acid.

By substituting various groups into a molecule it is possible to add hydrogen to different parts of a molecule. In the same way by adding certain hydrogen acceptors, i.e., substances which are capable of adding hydrogen, together with the catalyst, it is possible to remove hydrogen from different parts of a molecule.\*

*Synthesis of methanol.* One of the outstanding developments in industrial chemistry has been the large-scale production of methyl alcohol from carbon monoxide and hydrogen using a zinc oxide-

\* Adkins, "The Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937.

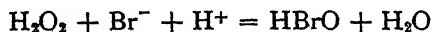
chromium oxide mixture as a catalyst.\* The reaction is easily controlled, and the catalyst is not easily poisoned. Pressures up to 200 atm. and temperatures between 200 and 400° are ordinarily used. Some of the higher alcohols have been synthesized in a similar manner, but it becomes increasingly difficult to suppress side reactions with the more complex molecules.

*Petroleum Products.* The most striking recent developments in catalysis have been made in the field of petroleum chemistry. Large-scale plants are now producing from ordinary petroleum a wide variety of products including toluene, butadiene for artificial rubber and isooctane and other compounds with high anti-knock properties. Moreover, through this catalytic cracking it has been possible to increase greatly the amount of gasoline obtainable from the petroleum.

*Enzymes.* Many chemical reactions in living organisms are catalyzed by complex organic substances called enzymes produced by the living cell. They are complicated proteins having molecular weights of more than 50,000 and many of them have been isolated in apparently crystalline form. When isolated they can carry on the same specific reactions in the laboratory (in vitro) as well as in the living organism (in vivo). *Catalase* exists in plant juice and in blood. It brings about the rapid decomposition of hydrogen peroxide.

Dextrose is fermented to give ethanol and carbon dioxide by the enzyme *zymase* which is present in yeast. The enzyme *urease* catalyzes the hydrolysis of urea, to give ammonium bicarbonate and ammonium hydroxide. Before the process of digestion can proceed, starch must be changed into sugar. This transformation is accelerated by an enzyme called *ptyalin* occurring in the saliva, and by other enzymes found in the pancreatic juice. The digestion of albumin is hastened by the enzymes *pepsin* and *trypsin*. Enzymes are very sensitive to traces of certain toxic substances such as hydrocyanic acid, iodine, and mercuric chloride.

*Decomposition of hydrogen peroxide.* Other catalytic reactions are effected through a catalytic pair which is alternately oxidized and reduced. An example is the bromine-bromide catalysis of the hydrogen peroxide decomposition.† In acid solutions bromide ion is oxidized to hypobromous acid by hydrogen peroxide according to the equation



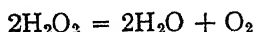
\* Fenske and Frolich, *Ind. Eng. Chem.*, **21**, 1052 (1929); Smith and Hirst, *ibid.*, **22**, 1037, 1040 (1930).

† Bray and Livingston, *J. Am. Chem. Soc.*, **45**, 1251 (1923).

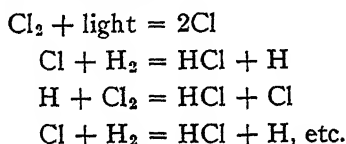
and the hypobromous acid in turn is reduced by hydrogen peroxide according to the equation



The second reaction is faster than the first, but eventually a *steady state* is reached in which the concentrations of bromide ion, hypobromous acid, and hydrogen ion are constant and the only apparent change is



**Chain Reactions.** The chain theory was first proposed by Bodenstein and by Nernst to account for the large yield obtained in the photochemical combination of chlorine and hydrogen to give hydrochloric acid. The reaction appears to be as follows:



This cycle continues in some cases until over a million molecules have reacted. The chains can be started by other means than light; for example, by bombardment with alpha particles from radium, or by reaction with traces of sodium vapor, or by a spark.

One may ask why such a reaction ever stops. At times, as a matter of fact the chain reaction does not stop until the material is consumed. At other times, however, the chain is broken when one of the activated molecules in the chain collides with the wall of the containing vessel or with foreign material which may be present as an impurity.

Certain oxidations in the gas phase have been explained successfully on the basis of chain reactions. The specific velocity of the reaction depends among other things on the size of the vessel, the pressure on the gases, and the temperature. The various factors have been expressed mathematically by Semenov\* in studies on the oxidation of phosphorus vapor and sulfur vapor. If at any time the generation of heat in the reaction becomes greater than the rate at which the heat is dissipated to the vessel, the chains become infinite in length and an explosion is produced. The explosion is prevented if the energy is dissipated with sufficient rapidity by radiation to the walls, by collision with walls and inert molecules, or by collision with molecules which react chemically without perpetuating the chain. The chains are stopped by colliding with the walls of the vessel as shown in the

\* Semenov. *Chem. Rev.*, 6, 347 (1929).

oxidation of phosphorus. The explosion can be stopped by reducing the pressure. Under these conditions the mean free path is longer and the activated molecules reach the walls more often. The length of the chain is equal to the total number of molecules of product obtained, divided by the number of chains started, and it may be measured in some cases by photochemical means as described later in Chapter XX.

Sometimes it is difficult to distinguish a chain reaction from an ordinary reaction and, in fact, the conditions may be such that the overall reaction appears to give a fairly good first- or second-order reaction. Certain foreign materials called *inhibitors* may retard a chain reaction greatly. If each molecule of the inhibitor stops a chain and each chain contains a great many molecules, it is obvious that mere traces of inhibitors are sufficient. For example, the oxidation of sodium sulfite by atmospheric oxygen is inhibited markedly by the addition of traces of alcohols.\* Lead tetraethyl in gasoline is another example of an inhibitor. Under certain conditions the chain reactions become too violent in a combustion engine and a "carbon knock" is produced. A trace of the volatile lead compound is sufficient to stop the chains and prevent the knock.

Still another example of the use of inhibitors is found in the preservation of gasoline. Certain unsaturated compounds in the gasoline tend to polymerize and form gums in the presence of air and light. Indophenol,  $\alpha$ -naphthol and certain other oxidizable substances containing phenolic and aromatic amine groups are effective in inhibiting this reaction.† Anti-oxidants are becoming important also in preserving foods.

**Free Radical Chains.** In the decomposition of organic substances at high temperatures free radicals such as  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{OH}$ ,  $\text{H}$ , and  $\text{Br}$  are formed, and they may propagate chain reactions. There is adequate evidence in band spectra for the existence of these free radicals which violate the rules of classical valence theories. Again their presence is revealed by the chemical removal of thin metallic mirrors. They are short-lived not because they are unstable but because they are extremely reactive. With these free radicals it is possible to set up a series of chain reactions in such a way that the overall reaction is first order or second order or fractional order; and it is possible that they may play an important part in the mechanism of several reactions.‡

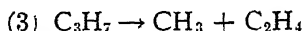
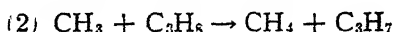
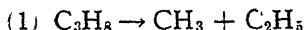
\* Alyea and Bäckström, *J. Am. Chem. Soc.*, **51**, 90 (1929).

† Egloff, Mowry, Lowry, and Dryer, *Ind. Eng. Chem.*, **27**, 413 (1935).

‡ Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.



For example, the thermal decomposition of a hydrocarbon, such as propane may involve the initial breakdown into free radicals, thus:



The  $\text{CH}_3$  then continues as before

(2')  $\text{CH}_3 + \text{C}_3\text{H}_8 \rightarrow \text{CH}_4 + \text{C}_3\text{H}_7$ , etc., and the chain may be ended by a combination of free radicals



Other reactions go on also, but these will illustrate the possibilities and explain how it is possible to obtain methane, ethylene, and butane among the products.

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### PROBLEMS

1. In a certain first-order reaction, half of the material is decomposed in 1000 seconds. (a) How long will it be until only one-tenth is left? (b) How many seconds are required for the reaction to be 99 per cent completed?

Ans. (a) 3322 sec. (b) 6643 sec.

2. From the following kinetic data on the rearrangement of 1-cyclohexenyl allyl-malononitrile at 135.7°, determine graphically the first-order reaction rate constant in reciprocal minutes. Check the graphical evaluation by calculating  $k$  from two different times.

Time (min.)	0	5	10	20	30	45
Per cent rearranged	19.8	34.2	46.7	64.7	77.0	86.3

Ans. 0.00068 sec.<sup>-1</sup>

3. A certain substance *A* is mixed with equal quantities of substances *B* and *C*. At the end of 1000 seconds half of *A* has reacted. How much will be left unreacted at the end of 2000 seconds if the reaction with respect to *A* is (a) first-order; (b) second-order in which equal parts of *A* and *B* react; (c) third-order in which equal parts of *A*, *B* and *C* react; (d) zero order?

Ans. (a) 0.25. (b) 0.33. (c) 0.35. (d) 0.0.

4. The following specific reaction rates were obtained by Wiig for the first-order decomposition of acetone dicarboxylic acid in aqueous solution.

$t^\circ$	0	20	40	60
$k \times 10^5$	2.46	47.5	576	5480

(a) Plot  $\log k$  against  $1/T$  and determine the energy of activation.

(b) Evaluate the constant  $s$  in the equation  $k = se^{-\Delta H_a/RT}$ .

(c) What is the period of half-life of this reaction at  $100^\circ$ ?

Ans. (a) 23,200. (b)  $9.1 \times 10^{13}$ . (c) 0.30 sec.

5. Hydrogen is contained in a vessel at 1 mm. pressure and  $25^\circ$ . Calculate: (a) the number of collisions on the walls per second per square centimeter; (b) the number of collisions between molecules per second per cubic centimeter; (c) the mean free path.

Ans. (a)  $1.44 \times 10^{21}$ . (b)  $2.73 \times 10^{21}$ . (c) 0.0114 cm.

6. If a unimolecular reaction has an activation energy of 25,000 cal. per mole and in the equation  $k = se^{-\Delta H_a/RT}$   $s$  has a value of  $5 \times 10^{13}$ , at what temperature will the reaction have a half-life of (a) 1 minute; (b) 1 month of 30 days?

Ans. (a)  $76^\circ$ . (b)  $-4^\circ$ .

7. The following data were obtained for the inversion of cane sugar where  $\alpha_t$  is the reading of the polarimeter at time  $t$ .

$t_{\min}$	0	10	20	40	80	180	300	$\infty$
$\alpha_t$	6.60	6.17	5.79	5.00	3.71	1.40	-0.24	-1.98

The reading  $\alpha_\infty$  corresponds to the completion of the reaction, and  $\alpha_t - \alpha_\infty$  is a measure of the sucrose remaining at any time. The  $\alpha_\infty$  has a negative sign because the products, fructose and glucose, rotate polarized light in the opposite direction. Calculate  $k$  in reciprocal seconds (a) by formula; (b) by plotting  $\log (\alpha_t - \alpha_\infty)$  against  $t$ .

8. A second-order reaction where  $a = b$  is 30 per cent completed in 10 minutes. How long will it take for the reaction to go to 50 per cent completion?

9. The specific rate of formation of hydriodic acid from its elements is 0.00025 at a certain temperature; the equilibrium constant at the same temperature is 0.0164. What is the specific rate constant of the reverse reaction?

10. Calculate from the data given in the text (a) the specific decomposition rate of nitrogen pentoxide and (b) the period of half-life at  $-15^\circ$ .

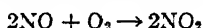
11. The decomposition of ethyl bromide is a first-order reaction with an activation energy of 54,800 cal. Estimate the temperature at which (a) ethyl bromide decomposes at the rate of one-tenth of one per cent per second and (b) the decomposition is 90 per cent complete in one hour.  $s = 3.8 \times 10^{14}$ .

12. Calculate (a) the mean free path and (b) the number of collisions against the wall when 1 g. of iodine is placed in a previously evacuated 1-liter, spherical flask and heated to  $100^\circ$ .

13. In a unimolecular decomposition the activation energy is 30,000 cal. per mole. (a) Calculate the fraction of molecules which have energy equal to or greater than this activation energy at  $100^\circ$ . (b) Calculate how many molecules have 30,000 cal

per mole of activation energy or more, when one-tenth of a mole of the material is heated to 100°.

14. The velocity constant  $k$  expressed in moles per liter per second for the reaction



at 600° K. is  $6.63 \times 10^5$ ; at 645° K. it is  $6.52 \times 10^5$ . For the reverse reaction,  $k$  is 83.9 and 407 at these two temperatures.

(a) Calculate the equilibrium constants at the two temperatures.

(b) Calculate  $\Delta E$  for the reaction, i.e., the heat of reaction at constant volume.

(c) Calculate  $\Delta H$ , i.e., the heat of reaction at constant pressure. The experimentally determined value of  $\Delta H$  is  $-28,483$  cal.

(d) Calculate the activation energy  $\Delta H_a$  for the forward and reverse reactions.

15. In the saponification of ethyl acetate by sodium hydroxide at 10°,  $y$  ml. of 0.056 molar hydrochloric acid was required to neutralize 100 ml. of the reaction mixture,  $t$  minutes after the commencement of the reaction.

$t$	0	4.89	10.37	28.18	$\infty$
$y$	47.65	38.92	32.62	22.58	11.48

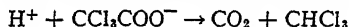
Calculate the specific reaction rate constant  $k$ , expressing the concentration in moles per liter and  $t$  in seconds.

16. The specific reaction rate  $k$  for the reaction



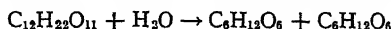
has a value of  $7.1 \times 10^9$  mole<sup>-2</sup> ml.<sup>2</sup> sec.<sup>-1</sup> at 25°. Air blown through a certain hot chamber and cooled quickly to 25° and 760 mm. contains 1 per cent by volume of nitric oxide and 20 per cent of oxygen. (a) How long will it take for 90 per cent of this nitric oxide, NO, to be converted into nitrogen dioxide, NO<sub>2</sub> (or N<sub>2</sub>O<sub>4</sub>)? (b) If the gases are blown through at the rate of 5000 cu. ft. per minute, how large a chamber must be constructed in order to obtain this 90 per cent conversion?

17. The trichloroacetate ion in hydrogen-containing ionizing solvents decomposes into carbon dioxide and chloroform according to the reaction



The unimolecular breaking of the carbon-carbon bond in the trichloroacetate ion is probably the rate-determining step. The reaction is first order and the specific rate constants are  $k_{30^\circ} = 3.11 \times 10^{-4}$ ,  $k_{38^\circ} = 7.62 \times 10^{-5}$ , and  $k_{70^\circ} = 1.71 \times 10^{-5}$  sec.<sup>-1</sup>. (a) Calculate the activation energy and (b) the specific rate constant at 60°. The experimentally determined value of  $k$  at 60° is  $3.48 \times 10^{-6}$ .

18. The following first-order reaction proceeds in the presence of hydrogen ions:



When this reaction was carried out in an aqueous solution, 0.1000 molar with respect to HCl, the following reaction rate constants were found at the temperatures indicated. Calculate graphically the energy of activation for the reaction given.

Temperature	$k$
21°	$4.42 \times 10^{-4}$
31°	$19.16 \times 10^{-4}$
41°	$73.5 \times 10^{-4}$

19. The thermal decomposition of gaseous acetaldehyde is a second-order reaction. The value of  $\Delta H_a$  is 45,500 cal. per mole, and the molecular diameter of the acetaldehyde molecule is  $5 \times 10^{-8}$  cm. (a) Calculate the number of molecules reacting per milliliter per second at 800° K. and 760 mm. pressure, and compare with the observed value  $7.3 \times 10^{16}$ . (b) Calculate  $k$  in moles per liter per sec. ( $k = -1/c^2 dc/dt$ ).

20. Write down a set of general equations in terms of  $M_1, M_2, M_3$ , etc., for different molecules and  $R_1, R_2$ , and  $R_3$ , etc., for different radicals, which can apply to the decomposition of organic molecules by a chain mechanism.

21. What are the units of  $k$ , the specific reaction rate constant, for a first-, second-, and third-order reaction?

22. The rearrangement of 1-cyclohexenyl allylmalononitrile into 2-allyl cyclohexylidene malononitrile can be followed by measuring the refractive index. The following first-order rate constants were observed:

$$\text{At } 120.00^\circ \quad k = 0.000181 \text{ sec.}^{-1}$$

$$\text{At } 130.00^\circ \quad k = 0.000409 \text{ sec.}^{-1}$$

$$\text{At } 140.00^\circ \quad k = 0.000914 \text{ sec.}^{-1}$$

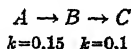
(a) Calculate the energy of activation.

(b) Calculate the value of the frequency factor at each temperature and determine the average value.

(c) Calculate the entropy of activation.

23. The reaction  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$  follows the third-order law. Assuming that a small amount of  $\text{N}_2\text{O}_2$  exists in rapid reversible equilibrium with  $2\text{NO}$ , and that the rate governing step is the slow bimolecular reaction  $\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2$ , show that the reaction will nevertheless appear to be third order.

24. Given the consecutive unimolecular reactions



plot curves which give the concentrations of  $A$ ,  $B$ , and  $C$  as a function of time.

25. Solve the following differential equation for  $k$ .

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$$

26. The energy of activation for the reaction  $\text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_4 + \text{HBr}$  is 55,000 cal. per mole. From this fact and Table III on page 121 show that the primary step in the dissociation cannot be the splitting off of a hydrogen atom nor a  $\text{CH}_3$  group but that it can involve the splitting off of an  $\text{HBr}$  molecule, or (considering the inaccuracy of the data) that it can involve the splitting off of a bromine atom.

27. A 3-liter container is filled with air at atmospheric pressure. In order to replace the air with carbon dioxide, the carbon dioxide is allowed to enter one end of the container at a rate of 2 liters a minute and gas is allowed to escape from the other end at the same rate. Assuming instant mixing of the gases, when will the partial pressure of oxygen be reduced to 0.01 mm.?

## CHAPTER XV

### ELECTRICAL CONDUCTANCE

**Historical Introduction.** Although early observations pointed to the probability of the existence of some relation between chemical and electrical phenomena, it was not until the beginning of the nineteenth century that electrochemistry had its birth. The discovery by Volta of a means of obtaining electrical energy from chemical energy gave the initial impulse to all the investigations upon which modern electrochemistry is based. Volta prepared a series of zinc and silver disks, arranged them alternately with paper soaked in salt water between them, and thus made a source of electricity available for experimentation.

In 1800 Nicholson and Carlisle decomposed water by electrolysis and Davy isolated alkali metals by means of an electric current. From his experiments Davy formulated an electrochemical theory, but this was soon superseded by the theories of Berzelius that every atom has both negative and positive charges, that the behavior of the atom is determined by the kind of electricity which is in excess, that chemical attraction is between oppositely charged atoms, and that the product formed by their union has the charge of the unneutralized electricity. Berzelius' theories were in turn superseded. There were times, however, when electrochemistry seemed to promise an explanation of all chemical reactions. But it was difficult to explain how negative chlorine atoms combine with each other to give chlorine molecules, or two positive hydrogen atoms combine to form hydrogen. It remained for recent theories of atomic structure to offer an explanation. Again it is only recently that the part played by electrical interaction in molecules having large dipole moments has been appreciated. The electron theory is important now in correlating some of the properties and reactions of organic molecules.

**Electrical Units.** In 1827 Ohm enunciated his well-known law of electrical conductance: *The magnitude of the electric current flowing in a conductor is directly proportional to the difference of potential between the ends of the conductor, and inversely proportional to its resistance.* If  $I$  represents the current,  $E$  the difference of potential, and  $R$  the resistance, then, with the proper choice of units, Ohm's law may be

formulated as follows:

$$I = \frac{E}{R} \quad [1]$$

The unit of resistance is the *ohm*; the unit of difference of potential, or electromotive force, is the *volt*; and the unit of current is the *ampere*. The international ohm is defined as the resistance offered to an unvarying current by a column of mercury at 0° C., 14.4521 g. in mass, 106.300 cm. in length, and of constant cross section. The international ampere is defined as the current which, under specified conditions, will cause the deposition of 0.001118 g. of silver per second from a solution of silver nitrate. The unit quantity of electricity is the *coulomb*. This amount of electricity passes when a current of 1 ampere flows for 1 second. The international volt is the potential difference which, when steadily applied to a conductor whose resistance is one international ohm, will produce a current of one international ampere.

As has already been pointed out, any form of energy may be considered as the product of two factors, a capacity factor and an intensity factor. The intensity factor of electrical energy is the volt; the capacity factor is the coulomb. Then

$$\text{Electrical energy in joules} = \text{Volts} \times \text{Coulombs}$$

Electrical energy may also be divided into a power factor, the *watt*, or *volt-ampere*, and a time factor, the second. One watt-second is 1 volt  $\times$  1 ampere  $\times$  1 second, or 1 joule. One kilowatt-hour is equal to 3,600,000 joules. The calorie is now defined in physical chemistry as 4.1833 international joules.\*

In addition to these practical units there are the electrostatic units, esu., and the electromagnetic units, emu., which are used in some theoretical work but are not ordinarily used in practical electrochemistry. If two equal charges 1 cm. apart in a vacuum repel each other with a force of 1 dyne, each charge is equivalent to 1 electrostatic unit. The electromagnetic unit of current is a current such that when it flows through a conductor 1 cm. long bent in an arc of 1 cm. radius, the force on a unit magnetic pole at the center of the circle will be 1 dyne.

**Electrical Conductance.** There are two different types of electrical conduction: metallic conduction as, for example, in a copper wire, and electrolytic conductance as, for example, in a solution of salt in

\* One international joule = 1.00020 absolute joules, page 657.

water. In metallic conductance the electricity appears to be a stream of electrons flowing toward the positive terminal. In electrolytic conductance electricity is carried in solution by ions. Positive ions move toward the negative electrode and negative ions move toward the positive electrode, and both share in carrying the current. In metallic conduction there is no change in the chemical properties of the conductor, but in electrolytic conductance, chemical reactions are produced at the electrodes and matter is transported to the electrodes.

Both types of electrical conductance involve the generation of more or less heat, depending on the electrical resistance of the system. As a general rule the metallic conductors become less conducting at high temperatures, whereas the electrolytic conductors become more conducting. In the former case, the electrons find it more difficult to pass through the crystal lattice when the units of the lattice are in thermal agitation; and in the latter case, the ions can move through the solution more readily because the viscosity is less and the solvation of the ions is less. In some cases the number of ion carriers is increased by an increase in temperature.

Electricity may be carried by electrons across an evacuated space as in an ordinary electron or radio tube. The electrons are emitted by a heated wire and drawn to a positively charged plate. Electricity may be carried also by means of gas ions, as in an electrical discharge. The gas ions are charged positively or negatively, and they move in a manner somewhat analogous to the movement of electrolytic ions. There are several points of difference, however. The gas ions may have several different charges and there is little connection between the valence and the charge, whereas in electrolytic ions the charge is closely connected with the valence. The electrolytic ions are present before the electrodes are charged, the large energy required for ionization being supplied from the solvation of the ions. Most of the gas ions, however, are produced only after the electrodes are charged, the energy required for ionization being supplied by collisions of charged particles in the electrical field. It is necessary to have a few gas ions to start with, but these are always present as a result of cosmic rays and traces of radioactive materials.

Electrical resistance is directly proportional to the length of the conductor and inversely proportional to its cross section. The specific electrical resistance (the resistance of a cube 1 cm. on an edge) of various materials is given for the sake of comparison in Table I.

In the neighborhood of absolute zero the resistance of metals be

comes extremely low. The specific resistance of mercury at 3° K., for example, is less than  $10^{-8}$  ohm.

TABLE I  
ELECTRICAL RESISTANCE OF TYPICAL CONDUCTORS

Material	Temperature	Specific Resistance
Silver	0°	$1.468 \times 10^{-6}$ ohm
Copper	0°	$1.561 \times 10^{-6}$
Aluminum	0°	$2.563 \times 10^{-6}$
Iron	0°	$9.065 \times 10^{-6}$
Lead	0°	$20.380 \times 10^{-6}$
Mercury	0°	$95.80 \times 10^{-6}$
Fused $\text{NaNO}_3$	500°	0.568
Fused $\text{ZnCl}_2$	500°	11.93
1 <i>M</i> KCl	25°	8.93
0.001 <i>M</i> KCl	25°	6,810.
1 <i>M</i> acetic acid	18°	757.5
0.001 <i>M</i> acetic acid	18°	24,400.
Water	18°	$2.5 \times 10^7$
Xylene	25°	$7 \times 10^{12}$

**Determination of Conductance of Solutions.** In the Wheatstone bridge shown in Fig. 110, *C* is the cell containing the solution whose resistance is to be measured, and *R* is a resistance box. The movable resistance coil at *ab* is moved so as to change the ratio *ad/bd* by multiples of ten. The resistance *R* is changed by turning dials which contact coils of resistance wires. Alternating current of about a thousand cycles, which gives a high mosquito-like noise in the telephone, *T*, is generated at *A*. A better type of cell for precision measurements is shown in the lower right-hand corner.

Alternating current is necessary to prevent complications at the electrodes. Direct current produces gas bubbles on the electrodes which greatly increase

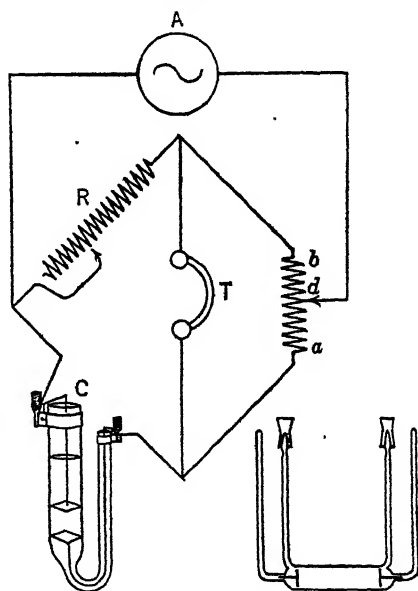


FIG. 110



the resistance and change the concentration of electrolytes in the neighborhood of the electrodes. If the alternating current is not of a pure sine-wave type with positive and negative potentials exactly offsetting each other, it is necessary to platinize the electrodes. This coating tends to adsorb the gases and catalyzes their reunion. The current may be generated with an electrically driven tuning fork or, better, with an oscillating circuit composed of radio tubes with proper capacities and inductances.

In making a measurement of the unknown resistance  $C$ , the known resistance  $R$  and the resistance ratio  $ad$  and  $bd$  are adjusted until the sound in the telephone is barely audible, i.e., the sound is at a minimum. Then the two terminals of the telephone are at the same potential and the potential drop  $E$  across the different parts of the bridge must be such that  $E_C = E_R$  and  $E_{ad} = E_{bd}$ . Moreover, since the drop in potential  $E$  is equal to the current  $I$  multiplied by the resistance  $R$

$$I_C C = I_R R \quad \text{and} \quad I_{ad} ad = I_{bd} bd$$

Dividing the first equation by the second

$$\frac{I_C C}{I_{ad} ad} = \frac{I_R R}{I_{bd} bd} \quad [2]$$

Furthermore,  $I_R = I_{bd}$  and  $I_C = I_{ad}$  since the current flowing through the two resistances in series must be the same in each resistance when no current flows through the telephone. Then cancelling out these equalities in equation (2)

$$\frac{C}{ad} = \frac{R}{bd}$$

or

$$\frac{C}{R} = \frac{ad}{bd} \quad [3]$$

This is the fundamental formula for the use of the Wheatstone bridge. In modern bridges the ratio  $ad/bd$  is arranged to give only 0.01, 0.1, 1, 10, 100, etc., so that no numerical calculations are necessary.

**Specific and Equivalent Conductance.** The *specific resistance* of an electrolyte may be defined as the resistance in ohms of a column of solution 1 cm. long and 1 sq. cm. in cross section. The *specific conductance*  $L$  is the reciprocal of the specific resistance. It is expressed in reciprocal ohms or *mhos*.

The *equivalent conductance*  $\Lambda$  is obtained by multiplying the specific conductance  $L$  by the volume  $V$  in milliliters which contains 1 g. equivalent of solute. i.e., by  $1000/c$  where  $c$  is the number of

gram equivalents per liter.

$$\Lambda = \kappa L = \frac{1000L}{c} \quad [4]$$

These relations may be illustrated by imagining a cell 1 cm. square and indefinitely high. Two opposite walls are of conducting metal which act as electrodes. When the cell is filled to a height of 1 cm. the conductance measured is the specific conductance. When to the hypothetical cell is added a solution containing one equivalent (the volume is  $V$  ml. and the height of solution is  $V$  cm.) the conductance measured is the equivalent conductance.

The term molar conductance is defined as in equation (4) except that the concentration is given in moles per liter instead of gram equivalents per liter.

In determining specific resistance it would be troublesome to prepare a cell having electrodes exactly 1 cm.<sup>2</sup> in area and exactly 1 cm. apart. However, it is not necessary to do this because it is possible to determine a factor, called the *cell constant*. The cell constant is determined experimentally with a standard solution of known specific conductance. Measurements on other solutions in any cell may then be converted directly into specific conductances. A 0.0200 molar solution of potassium chloride is generally used for the determination of the cell constant. It has the following specific conductances:

$$L_{18^\circ} = 0.002394 \quad \text{and} \quad L_{25^\circ} = 0.002768 \text{ reciprocal ohm}^*$$

If  $R$  is the resistance of the cell, when filled with 0.0200 molar potassium chloride,  $1/R$  is the conductance, and the specific conductance  $L$  is equal to  $k(1/R)$ , where  $k$  is the proportionality constant or cell constant, which converts measured conductance into specific conductance.

$$\text{Then} \quad k = LR \quad [5]$$

When the cell is filled with 0.0200 molar potassium chloride at 25°

$$k = 0.002768R$$

The cell constant  $k$  having been determined, the specific conductance of any solution is obtained from the measured resistance by the relation

$$L = \frac{k}{R} \quad [6]$$

\* The data of Jones and Bradshaw, *J. Am. Chem. Soc.*, **55**, 1780 (1933) are now taken as the standard for exact work in electrolytic conductance. When 0.745263 g. of pure potassium chloride is weighed out into pure water to give 1000 g. of solution (corrected to vacuum) the specific conductances are as follows: 0°, 0.0007736; 18°, 0.0012205; 25°, 0.0014087 mho. This solution contains 0.01 mole per cubic decimeter (which differs very slightly from a liter).

*Example 1.* When a certain conductance cell was filled with 0.02 *M* KCl it had a resistance of 82.4 ohms at 25° as measured with a Wheatstone bridge; and when filled with 0.0050 *N* K<sub>2</sub>SO<sub>4</sub> it had a resistance of 326 ohms.

(a) What is the cell constant?

$$k = 0.002768 \times 82.4 = 0.2281$$

(b) What is the specific conductance *L* of the potassium sulfate solution?

$$L = \frac{k}{R} = \frac{0.2281}{326} = 0.0006997$$

(c) What is the equivalent conductance?

$$\Lambda = 0.0006997 \times \frac{1000}{c} = \frac{0.6997}{0.0050} = 139.9 \text{ mho}$$

**Conductance of Different Electrolytes.** Table II gives the specific and equivalent conductances of aqueous solutions of potassium chloride at 25°.

TABLE II  
CONDUCTANCE OF POTASSIUM CHLORIDE AT 25°

Equivalents per Liter <i>c</i>	Dilution ML. per Equivalent <i>V</i>	Specific Conductance <i>L</i>	Equivalent Conductance $\Lambda$
1	1,000	0.1119	111.9
0.1	10,000	0.01289	128.9
0.01	100,000	0.001413	141.3
0.001	10 <sup>6</sup>	0.0001469	146.9
0.0001	10 <sup>7</sup>	0.00001489	148.9

It will be observed that when the volume is increased tenfold and the number of equivalents per milliliter is decreased to one-tenth, the specific conductance decreases nearly but not quite to one-tenth its value. The equivalent conductance on the other hand changes only slightly but does increase and approaches a limiting value at greater dilutions.

In very dilute solutions of potassium chloride there is no appreciable change in equivalent conductance when the solution is diluted with an equal volume of water. Although the volume is doubled and the number of ions per milliliter is halved, the *total* number of ion carriers is still the same. In more concentrated solutions of potassium chloride, however, the equivalent conductance increases on dilution because the ions move faster when they are farther apart and are not held back by ions of opposite charge which they tend to drag along.

In solutions of acetic acid the situation is quite different and the

equivalent conductance increases markedly on dilution because the solute dissociates more at the greater dilution giving a considerable increase in the total number of ions, i.e., the number of the carriers of electricity.

Electrolytes may be divided into two general classes: the *strong electrolytes*, such as potassium chloride, with high conductances and slight increases on dilution; and *weak electrolytes* such as acetic acid with low conductances and larger increases in conductance on dilution. In general, the strong electrolytes include many inorganic acids such as hydrochloric and sulfuric acid, most salts, and the alkaline hydroxides. The weak electrolytes on the other hand include the carboxylic acids and many organic acids and bases.

Table III gives the equivalent conductances of several typical electrolytes, from normal down to so-called "zero" concentration. For these electrolytes it will be observed that the equivalent conductance increases with the dilution of the solution until a limiting value,  $\Delta_0$ , is reached. It is important to bear in mind that, although  $\Delta_0$  is frequently referred to as the conductance at infinite dilution, it is by no means identical with the conductance of the pure solvent.

TABLE III  
EQUIVALENT CONDUCTANCES OF ELECTROLYTES AT 25°

Equiva- lents per liter ( <i>N</i> )	NaCl	KCl	HCl	NaOH	AgNO <sub>3</sub>	CaCl <sub>2</sub>	LaCl <sub>3</sub>	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>1</sup>
0.0000	126.5	149.9	426.1	248	133.4	135.8	145.9	91.0	(390.7)
0.0005	124.5	147.8	422.7	246	131.4	131.9	139.6	89.2	67.7
0.001	123.7	146.9	421.4	245	130.5	130.4	137.0	88.5	49.2
0.005	120.6	143.5	415.8	240	127.2	124.2	127.5	85.7	22.9
0.01	118.5	141.3	412.0	237	124.8	120.4	121.8	83.8	16.3
0.02	115.8	138.3	407.2	233	121.4	115.6	115.3	81.2	11.6
0.05	111.1	133.4	399.1	227	115.2	108.5	106.2	76.9	7.4
0.10	106.7	129.0	391.3	221	109.1	102.5	99.1	72.8	5.2

<sup>1</sup> Acetic acid is a weak electrolyte, and the conductance at infinite dilution is obtained by indirect methods. All the other electrolytes given in the table are strong electrolytes.

Conductance data are shown graphically in Fig. 111, where it will be noted that the equivalent conductance of the strong electrolytes such as hydrochloric acid reaches a limiting value at the higher dilutions. The weak electrolytes, such as acetic acid, however, do not reach such a limiting value within regions which can be studied experimentally. Below concentrations of 0.0001 molar the con-

ductance of the solvent itself becomes relatively large and traces of carbon dioxide or ammonia from the air, or alkali from the glass, introduce large errors.

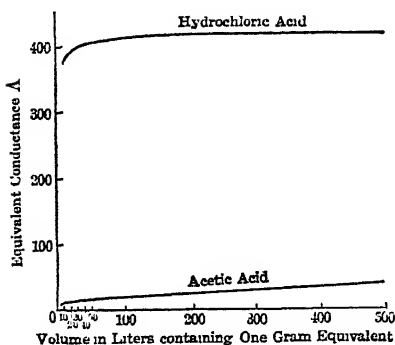


FIG. 111

When the equivalent conductance of strong electrolytes is plotted against the square root of the concentration, the line is nearly straight at the low concentrations as shown in Fig. 112. Extrapolation of this line to infinite dilution gives an accurate value of  $\Lambda_0$ . A weak electrolyte on the other hand gives steep curves which cannot be extrapolated to infinite dilution. The

values at infinite dilution must be determined indirectly as shown later on page 408. This equivalent conductance at infinite dilution is important in calculating the degree of dissociation of a weak electrolyte as shown on page 473.

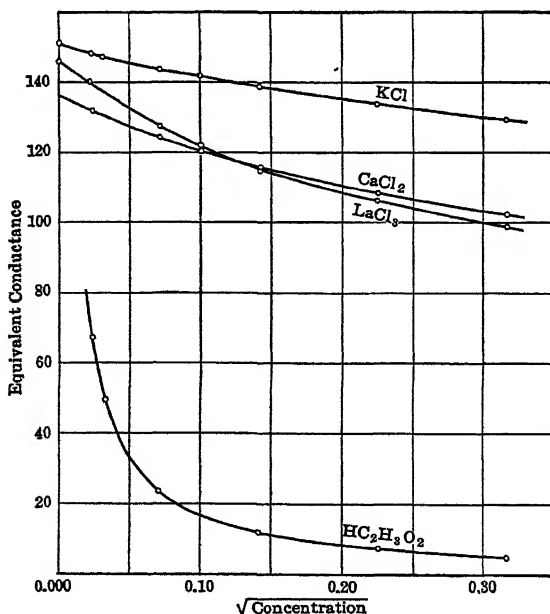


FIG. 112

**Faraday's Law.** When two electrodes of platinum or other inert metal are connected to a battery and immersed in an aqueous solu-

tion of salt, hydrogen is evolved at the negative electrode and oxygen at the positive electrode. If the solution is previously colored with a few drops of a solution of litmus, it will be observed that the solution in the neighborhood of the positive electrode turns red, indicating the formation of an acid, while that in the neighborhood of the negative electrode turns blue, showing the formation of a base. The same changes take place whether the electrodes are placed near together or far apart and, furthermore, the formation of gas and the change in color at the electrodes commence as soon as the circuit is closed. The study of these phenomena led Faraday in 1834 to the conclusion that, when an electric current traverses a solution, there occurs an actual transfer of matter, one portion traveling with the current, and the other portion moving in the opposite direction. Faraday termed these carriers of the current, *ions*. He called the electrode connected to the positive terminal of the battery, the *anode*, and the electrode connected to the negative terminal, the *cathode*. The ions which move toward the anode he called *anions*; those which migrate toward the cathode he called *cations*. The whole process he termed *electrolysis*. As a result of his experiments he enunciated the following laws:

(1) For the same electrolyte, the amount of electrolysis is proportional to the quantity of electricity which passes.

(2) The amounts of substances liberated at the electrodes, when the same quantity of electricity passes through solutions of different electrolytes, are proportional to their chemical equivalents.

On the basis of very accurate experimental measurements, Faraday's law may now be stated as follows:

*In electrolysis, 96,500 coulombs of electricity produce a chemical change of 1 gram-equivalent.* For example, 96,500 coulombs (or ampere-seconds) will liberate 1.0081 g. of hydrogen, and it will deposit from solution 107.88 g. of silver, 63.57/2 g. of copper from cupric salts, and 197.2/3 g. of gold from auric solutions. The name *faraday* and the symbol *F* are given to this important quantity of electricity.

This law is one of the most exact laws in physical chemistry; it has been found to hold at low and high temperatures, in dilute and concentrated solutions, at various pressures and in different solvents.

Faraday's law can be clearly understood with the help of the hypothesis that atoms are composed of positive nuclei surrounded by negative electrons. When an electron is removed from an atom, the remaining ion is positively charged. When an extra electron becomes attached to an atom, a negative ion is produced. If two electrons are involved, the ions are bivalent.

In electrolysis, electrons are supplied to the cathode and removed from the anode. This change is produced either by a chemical reaction in an external battery, or by the mechanical operation of a magnet in a dynamo. When cupric chloride is dissolved in water, each of the two chlorine ions holds an extra electron obtained originally from the copper atom. Every time two electrons are supplied to the cathode they become attached to one of the cupric ions which happens to be in contact with the cathode; an atom of copper is formed by the addition of two electrons to the cupric ion, which then deposits on the electrode. For every electron supplied to the cathode, one electron is withdrawn from the anode, and so it is obvious that the same amount of electrochemical action must occur at each electrode. At the anode the electrons are taken from the chloride ions in contact with the anode. Two chlorine atoms produced in this way from two chloride ions combine to give a chlorine molecule, which is liberated at the anode, or dissolved in the solution.

Electrolysis involves, then, a transfer of electrons between the electrodes and the surrounding ions, and Faraday's law is simply the result of counting off one electron for each univalent atom, or two electrons for each divalent ion, etc. Each gram-atom of a univalent element contains  $6.023 \times 10^{23}$  atoms, and accordingly  $6.023 \times 10^{23}$  electrons are involved in its electrolysis. The charge on the electron is  $1.602 \times 10^{-19}$  coulomb (Chapter XXII), and so the coulombs required to electrolyze a gram-atom of a univalent ion are

$$6.023 \times 10^{23} \times 1.602 \times 10^{-19} = 96,488^* \quad [7]$$

This number is in agreement with the value already given. As a matter of fact, the experimental determination of the value of the faraday and the charge on the electron provide one of our best means for determining the value for the Avogadro number,  $6.02 \times 10^{23}$ .

Since Faraday's law involves only a counting process, it is evident why the law is so exact. Its accuracy is limited only by the accuracy of measuring the chemical change and the quantity of electricity.

The quantity of electricity passing through an electric circuit can be measured by means of an electrolytic cell which is so arranged that the change taking place at an electrode is determined by chemical analyses. Such a cell is called a *coulometer*. The silver coulometer is the most accurate. In it the silver is deposited electrically from a solution of silver nitrate upon a weighed platinum dish.

\* This value is in absolute units. The more commonly used value 96,500 is in international units.

*Example 2.* A current of 0.100 amp. is passed through a copper sulfate solution for ten minutes using platinum electrodes.

(a) Calculate the number of grams of copper deposited at the cathode.

$$\frac{10 \times 60 \times 0.100}{96,500} \times \frac{63.57}{2} = 0.01976 \text{ g.}$$

(b) Calculate the number of atoms deposited.

$$\frac{10 \times 60 \times 0.100}{96,500} \times \frac{1}{2} \times 6.02 \times 10^{23} = 0.1872 \times 10^{23}$$

(c) Calculate the volume of oxygen liberated at the anode at 25° and 740 mm.

$$\frac{10 \times 60 \times 0.100}{96,500} \times \frac{16 \cdot 2}{32} \times \frac{82.06 \times 298.1}{740 \cdot 760} = 3.92 \text{ ml.}$$

(d) How much heat was evolved if the potential drop between the two electrodes was 10.00 volts?

$$\frac{10.00 \times (10 \times 60 \times 0.100)}{4.1833} = 143 \text{ cal.}$$

**Migration of Ions.** The current is carried through the wire by electrons but it is carried through the solution by positive ions moving toward the cathode and by negative ions moving toward the anode. It is not necessary that the two ions carry the same fractions of the current even though they may have the same valence. The fraction of the current carried through the solution is a function of the relative velocities with which the cation and the anion move. The ions which move faster carry the larger quantity of electricity across the solution in a given time, i.e., they carry the larger fraction of the current. If  $v_c$  is the relative velocity of the cation and  $v_a$  is the relative velocity of the anion, then the transference number  $n_c$  of the cation is the fraction of the current carried by the cation as given by the following equation

$$n_c = \frac{\text{Current carried by cation}}{\text{Total current}} = \frac{v_c}{v_c + v_a} \quad [8]$$

Likewise the transference number of the anion,  $n_a$ , is equal to  $v_a/(v_c + v_a)$ . It is obvious that

$$n_c + n_a = 1 \quad [9]$$

These fractions,  $n_a$  and  $n_c$ , called the *transference numbers*, were first investigated by Hittorf in 1853.

During electrolysis the concentration around the two electrodes is changed both by the chemical changes taking place at the electrodes



and by the migration of cations and anions. The way in which these changes are effected is illustrated diagrammatically in Fig. 113. The solution undergoing electrolysis is divided into three compartments

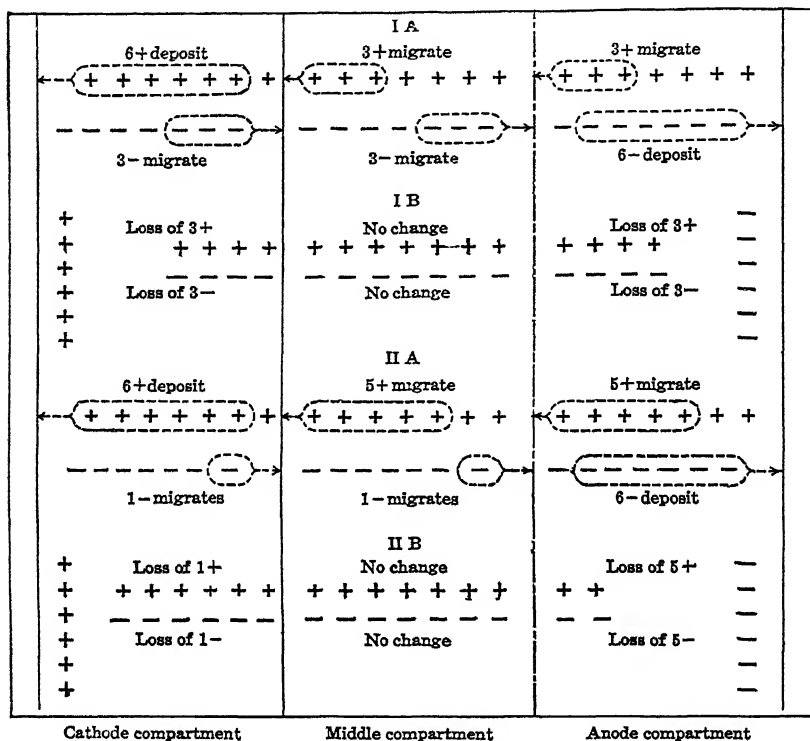


FIG. 113

with imaginary partitions. The concentration is uniform throughout the vessel before the electrolysis, and it is assumed for the sake of discussion that there are seven positive and seven negative ions in each compartment, and that the current is passed long enough to deposit six ions. Six electrons are removed from the anode and supplied to the cathode, and accordingly six cations are discharged at the cathode and six anions are discharged at the anode.

In the first case shown in Fig. 113 it is assumed that the cations and anions have the same velocity and each carries half the current. Accordingly three positive charges are carried between the electrodes by the cations, and three negative charges are carried in the opposite direction by the anions. The movement of the ions is indicated by dotted arrows in IA and the net result is shown in IB. Six cations

have been deposited at the cathode, three have moved into the cathode compartment from the middle compartment, and three have moved into the middle compartment from the anode compartment. Similar changes have occurred with the anions. The net result of migration and electrolysis is to decrease the concentration in the neighborhood of the electrodes from seven to four and to leave the concentration unchanged in the middle compartment.

When the transference numbers of the two ions are not equal, the change in concentration is different at the two electrodes as shown at IIA and IIB. In hydrochloric acid, for example, the hydrogen ion travels about five times as fast as the chloride ion, and at room temperature,  $n_c = 0.83$  and  $n_a = 0.17$ . Six ions are discharged at each electrode as before, but in this case five-sixths of the current is carried by the hydrogen ion and one-sixth by the chloride ion. The changes are indicated by dotted lines and arrows in IIA and the net result is shown in IIB. Six hydrogen ions are discharged at the cathode, but five move in from the middle compartment, giving a net loss of one hydrogen ion. There is also a loss of one chloride ion due to migration. Six chloride ions are discharged at the anode, but only one migrates into the anode compartment and the net loss around the anode is five. There is also a loss of five hydrogen ions, owing to migration toward the cathode.

**Transference Numbers by Change in Concentration.** Transference numbers may be determined by measuring the change in concentration of an electrolyte due to the migrating ions. The number of gram-equivalents transported in this way divided by the total number of equivalents transported, as determined with a coulometer, gives at once the transference numbers,  $n_c$  and  $n_a$ , of the cation and anion, respectively.

$$n_c = \frac{\text{Change in equivalents due to migration of cation}}{\text{Total equivalents migrating (faradays)}} \quad [10]$$

and

$$n_a = \frac{\text{Change in equivalents due to migration of anion}}{\text{Total equivalents migrating (faradays)}} \quad [11]$$

The total change in number of equivalents around an electrode depends not only on migration but also on the chemical changes occurring at the electrodes, thus

$$\epsilon_{\text{final}} = \epsilon_{\text{initial}} \pm \epsilon_{\text{electrode}} \mp \epsilon_{\text{migration}} \quad [12]$$

where  $\epsilon$  is the number of gram-equivalents of an ion. The number of equivalents initially present and the number finally present around

an electrode are determined by chemical analysis of a given sample of the solution. The sample is taken large enough to include all the solution in the immediate neighborhood of the electrode.

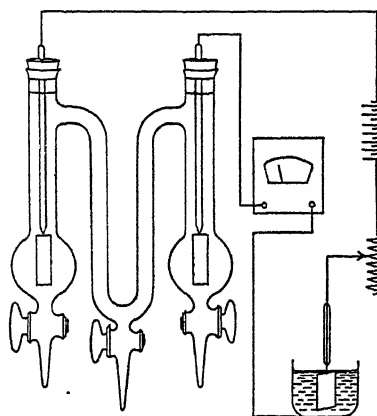


FIG. 114

An apparatus for determining transference numbers by this method is shown in Fig. 114. A voltage of about 50 to 100 volts is controlled with a rheostat so as to pass through the solution a constant current of a few milliamperes. The exact quantity of electricity is obtained from the coulometer at the right; and the solutions around the cathode and anode are analyzed. The analysis of the middle compartment gives the initial concentration because there is no

change in it during electrolysis. The number of equivalents per gram of water is multiplied by the number of grams of water taken in the sample. The calculation of the number of equivalents before and after the electrolysis in each case must be made on the basis of the same weight of water.

Equation (12) is readily solved for the number of equivalents brought into the compartment or removed from it by the migration. If the concentration of the ion is increased by the migration, as when a positive ion is moving into the cathode chamber,  $\epsilon_{\text{migration}}$  has a positive value. Some chemical knowledge is necessary to determine the sign of  $\epsilon_{\text{electrode}}$ . For example, if a copper anode is used there will be solution of the electrode and an increase in the concentration of copper in the anode compartment, while if a platinum anode is used in a copper solution  $\epsilon_{\text{electrode}}$  for the copper ion will be zero. In the solution at the cathode,  $\epsilon_{\text{electrode}}$  will have a negative value because the copper is removed from solution.

After calculating the part of the change in concentration which is actually due to migration, it is easy to determine the transference number using either equation (10) or (11).

*Example 3.* An aqueous solution of copper sulfate was electrolyzed between copper electrodes. On the cathode 0.3000 g. of copper was deposited. The solution in the anode compartment contained 1.4300 g. of copper after electrolysis, and the same weight of water originally contained 1.2140 g. before electrolysis. Calculate the transference numbers of the ions.

For the  $\text{Cu}^{++}$  cation

$$\begin{aligned}\epsilon_{\text{final}} &= \epsilon_{\text{initial}} + \epsilon_{\text{electrode}} - \epsilon_{\text{migration}} \\ \frac{1.4300}{31.78} &= \frac{1.2140}{31.78} + \frac{0.3000}{31.78} - \epsilon_{\text{migration}} \\ \epsilon_{\text{migration}} &= \frac{0.084}{31.78} \\ n_{\text{Cu}^{++}} &= \frac{0.084/31.78}{0.300/31.78} = 0.28 \\ n_{\text{SO}_4^{--}} &= 1.00 - 0.28 = 0.72\end{aligned}$$

Table IV gives the transference numbers of the cations of several typical electrolytes, at different concentrations. The transference numbers of the corresponding anions can be found by subtracting the transference numbers of the cations from unity.

TABLE IV  
TRANSFERENCE NUMBERS OF CATIONS AT 25°

Electrolyte	0.01 <i>N</i> <sup>1</sup>	0.05 <i>N</i>	0.1 <i>N</i>	Electrolyte	0.01 <i>N</i> <sup>1</sup>	0.05 <i>N</i>	0.1 <i>N</i>
HCl	0.825	0.829	0.831	AgNO <sub>3</sub>	0.465	0.466	0.468
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	0.554	0.557	0.559	LaCl <sub>3</sub>	0.462	0.448	0.437
KNO <sub>3</sub>	0.508	0.509	0.510	K <sub>3</sub> Fe(CN) <sub>6</sub>	0.431	0.439	0.441
NH <sub>4</sub> Cl	0.491	0.491	0.491	CaCl <sub>2</sub>	0.426	0.414	0.406
KCl	0.490	0.490	0.490	NaCl	0.392	0.388	0.385
KBr	0.483	0.483	0.483	LiCl	0.329	0.321	0.317

<sup>1</sup> Equivalents per liter.

The transference numbers vary slightly with the concentration. They depend on the relative ionic diameters and particularly on the extent to which the ions are solvated. Those ions which are extensively solvated, such as calcium and lithium, move slowly on account of the extra solvent molecules which they must drag along. With rising temperature there is a slight tendency for the ions with the most water of hydration to lose the most. This tends to equalize the velocities and bring the transference numbers more closely to the limiting value of 0.5 at higher temperatures.

The fact that ions are hydrated may be shown by an experiment on transference numbers in which sugar is added to the solution.\* The sugar is not moved by the potential gradient but when the solution around the electrodes is examined with a polarimeter the concentration of sugar becomes less in the compartment into which the

\* Washburn and Millard. *J. Am. Chem. Soc.*, **37**, 694 (1915).

hydrated ions migrate. The solution becomes diluted by the water dragged along with the ion.

Hydrogen ions and hydroxyl ions possess abnormally high velocities in water, possibly because the proton can be transferred from molecule to molecule.

**Ionic Mobilities.** The absolute velocity of ions may be determined directly by measuring the distance traveled in a given period of time under a definite potential gradient. A solution of one electrolyte is carefully floated on top of another in a long tube of uniform diameter and the distance between the electrode and the applied voltage is measured. A line of demarcation between a colored and a colorless solution provides the simplest means of observation, but uncolored ions may be traced by the absorption of ultraviolet light or by the distortion of a scale viewed through the boundary between the two liquids where there is an abrupt change in refractive index. In order to keep the boundary sharp the two ions are chosen so that the slower ion follows the faster ion. Mechanical stirring is avoided by selecting electrodes which will give no evolution of gas as, for example, cadmium or silver-silver chloride electrodes in a chloride solution.

The velocities of ions are summarized in Table V where the mobilities are given in centimeters per second at 25° under a potential gradient of 1 volt per centimeter.

TABLE V  
IONIC MOBILITIES AT 25°

Ion	Mobility	Ion	Mobility	Ion	Mobility	Ion	Mobility
H <sup>+</sup>	0.00362	Cl <sup>-</sup>	0.00079	Ba <sup>++</sup>	0.00066	HCO <sub>3</sub> <sup>-</sup>	0.00046
OH <sup>-</sup>	0.00205	K <sup>+</sup>	0.00076	Cr <sub>2</sub> O <sub>7</sub> <sup>---</sup>	0.00054	Li <sup>+</sup>	0.00040
SO <sub>4</sub> <sup>---</sup>	0.00083	NO <sub>3</sub> <sup>-</sup>	0.00074	Na <sup>+</sup>	0.00052	Cu <sup>++</sup>	0.00036

It will be noted that aside from the hydrogen and hydroxyl ions most of the ions have velocities of the order of  $3 \text{ to } 8 \times 10^{-4}$  cm. per sec. or about 2 cm. per hr. at 25° under a potential gradient of 1 volt per cm.

**Transference Numbers by Moving Boundary.\*** Transference numbers may be determined in a manner similar to that just described for measuring ionic mobilities. As shown in Fig. 115, two solutions with different colors or refractive indices are placed in a tube which is graduated in fractions of milliliters. When a voltage is applied

\* MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp.,

to the electrodes the movement of the boundary  $B$  is observed and the volume swept out by the moving ion is recorded.\* In Fig. 115 the upper electrode is of silver-silver chloride and the lower electrode is of cadmium. The tube is filled with hydrochloric acid and an indicator. When the circuit is closed, the fast hydrogen ions move upward, followed by the slower cadmium ions produced at the anode, and the acid color of the indicator marks sharply the boundary between the two. The current of about 5 to 10 ma. is kept constant by regulating the adjustable rheostat.

If  $c$  equivalents of the electrolyte (hydrochloric acid in this case) is dissolved in a liter of solution, the volume in milliliters containing 1 gram-equivalent is  $1000/c$ . When 1 faraday  $F$  of electricity passes through the solution there will be a movement of 1 equivalent of electrolyte, or  $1000/c$  ml. of solution. Of this volume of solution  $n_c(1000/c)$  ml. will be swept out by the cation and  $n_a(1000/c)$  ml. by the anion. If a smaller quantity of electricity  $f$  is passed, a smaller volume,  $v$  ml., will be swept out by the cation and measured in the graduated tube. Then

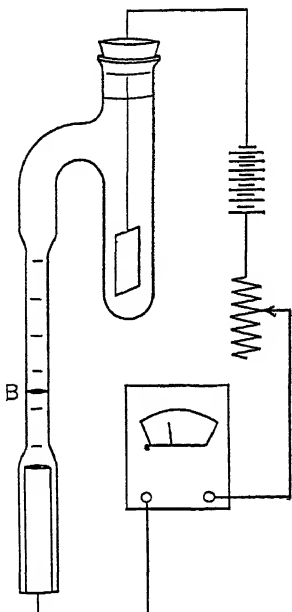


FIG. 115

$$\frac{f}{F} = \frac{v}{n_c(1000/c)} \quad [13]$$

Since the current is kept constant the number of coulombs  $f$  is equal to the time  $t$  in seconds multiplied by the current  $i$  in amperes. Then

$$n_c = \frac{vFc}{1000ti} \quad [14]$$

A similar formula may be derived for the anion.

*Example 4.* In a vertical moving boundary apparatus for transference numbers the cathode was placed at the top. The anode at the bottom was surrounded by lithium chloride; on top of this solution was sodium chloride solution, and on top of that was sodium acetate surrounding the cathode. The sodium ion moves faster than the lithium ion and the chloride ion moves faster than the

\* MacInnes and Longworth, *J. Am. Chem. Soc.*, **60**, 3070 (1938); Longworth, *J. Chem. Education*, **11**, 420 (1934).

acetate ion. If the chloride-acetate boundary moved down 8.06 mm. while the sodium-lithium boundary moved up 4.94 mm., calculate the transference numbers of chloride and sodium ions. Since the charge on each ion, the current, the time, the cross section of the tube, and the concentration were the same for the two ions,

$$n_a = \frac{8.06}{8.06 + 4.94} = 0.62 \quad \text{and} \quad n_c = \frac{4.94}{4.94 + 8.06} = 0.38$$

**Ionic Conductances.** As early as 1875 Kohlrausch examined the equivalent conductances of many different electrolytes, and came to the conclusion that *at infinite dilution* the ions behave independently so that the equivalent conductance of the electrolyte  $\Lambda_0$  is equal to the sum of the equivalent conductances of the cations  $l_{0,c}$  and anions  $l_{0,a}$ , thus

$$\Lambda_0 = l_{0,c} + l_{0,a} \quad [15]$$

This law of Kohlrausch is supported, for example, by the fact that

$$^* \Lambda_{0,KCl} - \Lambda_{0,NaCl} = 149.9 - 126.4 = 23.5$$

$$\Lambda_{0,KI} - \Lambda_{0,NaI} = 150.3 - 126.9 = 23.4$$

This constant difference of about 23.4 mhos is always found between a potassium and a sodium salt of the same acid at infinite dilution. It is easily explained on the basis that the conductance of the potassium ion is 23.4 more than that of the sodium ion, that the anion is the same in both cases, and that the conductance depends only on the presence of the independent ions.

Kohlrausch's law is useful in calculating the equivalent conductance at infinite dilution of the weak electrolytes which cannot be determined by direct extrapolation.

*Example 5.* Calculate the equivalent conductance of acetic acid at infinite dilution. Extrapolation gives the following values at infinite dilution,

$$\Lambda_{0,HCl} = 426.0; \Lambda_{0,NaC_2H_3O_2} = 91.0 \text{ mhos}; \Lambda_{0,NaCl} = 126.4$$

$$(l_{0,H^+} + l_{0,Cl^-}) + (l_{0,Na^+} + l_{0,C_2H_3O_2^-}) - (l_{0,Na^+} + l_{0,Cl^-}) = l_{0,H^+} + l_{0,C_2H_3O_2^-}$$

$$\Lambda_{0,HCl} + \Lambda_{0,NaC_2H_3O_2} - \Lambda_{0,NaCl} = \Lambda_{0,HC_2H_3O_2}$$

$$\Lambda_{0,HC_2H_3O_2} = 426.2 + 91.0 - 126.5 = 390.7$$

The method of differences illustrated in this problem gives the equivalent conductances of a weak electrolyte, but it does not permit a calculation of the individual ionic conductances. They may be calculated, however, with the help of the transference numbers. At infinite dilution the transference number is the fraction of the total

current carried by the electrolyte, which in turn is the ratio of the conductance of the ion to the conductance of all the ions, i.e., to the conductance of the electrolyte.

Thus at infinite dilution

$$n_c = \frac{l_{0,c}}{l_{0,c} + l_{0,a}} = \frac{l_{0,c}}{\Delta_0} \quad [16]$$

and

$$l_{0,c} = n_{0,c} \times \Delta_0 \quad [17]$$

Also

$$l_{0,a} = n_{0,a} \times \Delta_0$$

With equations (15) and (17) it is possible to determine the equivalent conductances at infinite dilution of weak electrolytes.

*Example 6.* Calculate  $\Delta_0$  for acetic acid at 25°, using the data of Tables III and IV.

$$l_{0,H^+} = n_{0,c} \times \Delta_{HCl} = 0.82^* \times 426.1 = 349.4$$

$$l_{0,C_2H_3O_2^-} = n_{0,a} \times \Delta_{NaC_2H_3O_2} = 0.45^* \times 91.0 = 40.9$$

$$\Delta_{0,HCl} = l_{0,H^+} + l_{0,C_2H_3O_2^-} = 390.3$$

When the conductance of one ion at infinite dilution is determined, others may be obtained from the equivalent conductances of the electrolytes by simple subtraction, using equation (15). An average of several chlorides gives  $\Delta_{0,Cl^-}$  as 76.3 mhos. Then, for example

$$l_{0,K^+} = \Delta_{0,KCl} - l_{0,Cl^-} = 149.9 - 76.3 = 73.6$$

In this way Table VI has been constructed.

TABLE VI  
IONIC CONDUCTANCES AT INFINITE DILUTION AT 25°

Cations	$l_c$	$a$	Anions	$l_a$	$a$
H <sup>+</sup>	349.8	0.014	OH <sup>-</sup>	198	0.016
K <sup>+</sup>	73.5	0.019	$\frac{1}{2}\text{Fe}(\text{CN})_6^{4-}$	101.0	.....
NH <sub>4</sub> <sup>+</sup>	73.4	0.019	$\frac{1}{2}\text{SO}_4^{2-}$	79.8	0.020
$\frac{1}{3}\text{La}^{+++}$	69.6	.....	Br <sup>-</sup>	78.4	0.019
$\frac{1}{2}\text{Ba}^{++}$	63.6	0.020	I <sup>-</sup>	76.8	0.019
Ag <sup>+</sup>	61.9	0.020	Cl <sup>-</sup>	76.3	0.019
$\frac{1}{2}\text{Ca}^{++}$	59.5	0.021	NO <sub>3</sub> <sup>-</sup>	71.4	0.018
$\frac{1}{2}\text{Mg}^{++}$	53.1	0.022	HCO <sub>3</sub> <sup>-</sup>	44.5	.....
Na <sup>+</sup>	50.1	0.021	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	40.9	.....
Li <sup>+</sup>	38.7	0.023			

\* Extrapolated values.



The temperature coefficient is given under the columns  $a$ , where  $a$  is defined by the equation

$$I_{0,t} = I_{0,25}[1 + a(t - 25)]$$

for the ionic conductance at temperatures  $t$  not far removed from  $25^\circ$ . It will be noted that most of these values give an increase of about 2 per cent per degree which is about the same as the temperature coefficient of the viscosity of water. With this table it is easy to calculate equivalent conductances of many different electrolytes at infinite dilution, or to calculate transference numbers when the equivalent conductances are also known.

Each ion moving through the solution probably carries with it an atmosphere of solvent, and the frictional resistance offered to the motion of the ion is the frictional resistance between masses of pure water. This view is in harmony with other facts. According to this theory it would be expected that the most heavily hydrated ions would lose more of the water of hydration when heated and would have larger temperature coefficients of conductance. Hydrated electrolytes, which form crystals with water of crystallization, appear to give ions with small transference numbers. The increase with temperature of the conductance of weak electrolytes is due not only to the increased velocity but also to an increase in the degree of dissociation.

**Conductance of Nonaqueous Solutions.** In general, the conductance of pure liquids is small. Thus, the specific conductance of pure water, at  $25^\circ$ , is approximately  $5.5 \times 10^{-8}$  reciprocal ohm, and the specific conductance of a number of other solvents is of the same order as that of water. Whereas the purest water has a specific resistance of about 20 million ohms, it is difficult to obtain water with much over a million ohms specific resistance on account of the absorption of carbon dioxide and other gases from the atmosphere, and of alkali and other electrolytes from the glass-containing vessel. Ordinary distilled water in equilibrium with air has a specific resistance of only about 100,000 ohms.

Mixtures of two liquids, each of which is practically nonconducting, may have a conductance differing but little from that of the two components, or the mixture may have a very high conductance. For example, the conductance of a mixture of water and ethyl alcohol is of the same order of magnitude as that of the two components; on the other hand, a mixture of water and sulfuric acid is highly conducting, although in the pure state, each is practically a nonconductor. As the concentration of the sulfuric acid increases, the specific con-

ductance of the mixture increases until 30 per cent of acid is present, beyond which it diminishes. There is a minimum in the curve corresponding to about 85 per cent of acid, a concentration which corresponds almost exactly with the hydrate,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . After increasing again slightly, the conductance falls off, and approaches a very low conductance at 100 per cent sulfuric acid. On dissolving sulfur trioxide in the pure acid, the specific conductance increases slightly to a maximum, and then falls practically to zero.

When a given salt is dissolved in different solvents the conductance in general increases as the dielectric constant of the solvent increases, and decreases as the viscosity increases.

Crystalline salts are exceedingly poor conductors of electricity, but their conductance increases as the temperature is raised until at the melting points or just below they become good conductors. In the ionic crystal lattice, the ions are held in fixed positions by powerful electrostatic forces, but in the fused salt they are free to move. The specific conductance of a fused salt may even exceed the specific conductance of the most concentrated aqueous solution, but, owing to the high concentration of electrolyte, the equivalent conductance is much less.

Data on silver nitrate are given in Table VII. The specific conductance of a 50 per cent aqueous solution of silver nitrate, at  $18^\circ$ , is 0.208 reciprocal ohm.

TABLE VII  
CONDUCTANCE OF FUSED SILVER NITRATE

Temperature, Degrees	Specific Conductance	Equivalent Conductance
218 (melt. pt.)	0.681	29.2
250	0.834	36.1
300	1.049	46.2
350	1.245	55.4

If the salts are impure the conductance is greater, the effect of impurities being apparent even before the salts have reached their melting points. This is analogous to the behavior of solutions, and suggests that the impurity functions in the salt mixture as a dissolved solute.

Electrolysis in fused salts is a matter of technical importance, notably in the production of metallic aluminum from bauxite in fused cryolite.

**Conductance Titrations.** Since the conductance of a solution is dependent upon both the concentration and the speed of its ions, it

follows that any changes in either of these factors during a reaction will produce corresponding changes in the electrical conductance of the reaction mixture. In the neutralization of a strong acid by a strong base, the conductance of the acid will diminish as its highly mobile hydrogen ions are gradually replaced by the slower-moving cations of the base. Since the degree of ionization of the resulting salt is of the same order of magnitude as that of the acid, the conductance of the acid solution continues to decrease until the end point is reached and all the hydrogen ions have combined with the hydroxyl ions of the base. As soon as an excess of the base is added, however, the conductance begins to increase on account of the increase in the total number of ions, especially the increase in the number of fast-moving hydroxyl ions.

A typical experiment is shown in Fig. 116 where the conductances are plotted against the milliliters of base added to a given acid. The abscissa corresponding to the point *B* at which the two lines intersect is the end point. In order that *AB* and *BC* shall be straight lines it is necessary to keep the volume constant throughout the titration. In other words, the reagent must be concentrated, whereas the solution which is being titrated must be dilute. If these conditions are fulfilled, four readings corresponding to the points *A*, *D*, *E*, and *C* suffice to determine the end point in the titration of a strong acid by a strong base.

If the base is weak, the line *BC* is more nearly horizontal and the lines do not meet at such a sharp angle because, after the rapidly moving hydrogen ions are converted into water molecules, the conductance is small and the excess base does not contribute many hydroxyl ions inasmuch as it is only slightly ionized. This type of titration gives somewhat less accurate results.

The titration of a weak acid (boric acid) by a strong base (NaOH) is shown in Fig. 117. Boric acid is such a weak acid that its conductance is very slight. The sodium borate formed has a much higher conductance, but when the sodium hydroxide is in excess the slope of the line becomes steeper because of its still greater conductance. The end point is easily determined as the point where the slope changes.

In practical work it is usually more convenient to plot resistance or merely bridge readings instead of conductances against the buret readings.

Conductimetric titrations are useful in analyzing colored or turbid solutions in which the determination of the end point is often rendered uncertain owing to the masking of the indicator by the color of the solution. The conductance method may also be applied to the de-

termination of the end points of reactions involving precipitations; in fact, the method is often superior to the more familiar analytical procedures. It has been used, for example, in the precipitation of silver iodide and barium sulfate. One of the best reactions for this method is the precipitation of a bivalent metal sulfate with barium hydroxide, for in this case both the products are insoluble and the conductance at the end point is very low.

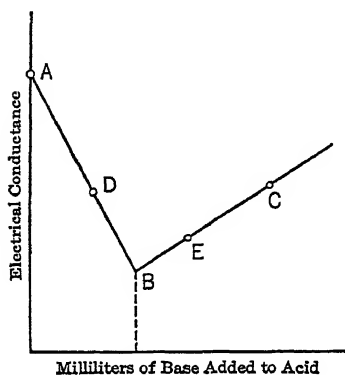


FIG. 116

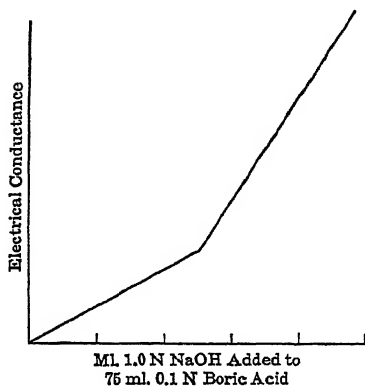
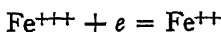
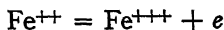


FIG. 117

**Electrolysis.** In discussing Faraday's law, it was shown that electrolysis involves the addition of electrons to the cathode and the removal of electrons from the anode. The addition of electrons is called *reduction* and the removal of electrons is called *oxidation*. Reduction occurs at the cathode, which is rendered negative by connecting to a dynamo or battery. Oxidation occurs at the anode. Thus in electrolysis, ferric ions are reduced to ferrous ions at the cathode:



and ferrous ions are oxidized to ferric ions at the anode:



Faraday's law gives the relation between the number of electrons passing through the electrode and the number of ions deposited or changed but it does not state which of several competing reactions will occur at the surface of the electrode nor whether or not there are secondary reactions which follow the primary change, the one involving the electron transfer. Some chemical experience is necessary in predicting just what will happen. For example, if chlorine is

liberated in an alkaline solution, hypochlorite or chlorate may be formed. If chlorine is liberated on a silver anode, silver chloride is formed.

If a copper anode is used in the electrolysis of a solution of cupric chloride, the copper will simply go into solution and take the place of that which is removed at the cathode. If a platinum anode is used, the platinum cannot go into solution and oxygen is liberated from the water. When several different ions are competing for the transfer of an electron, several possibilities occur, depending on the concentration and on the energies involved. If there are no easily reducible cations around the cathode, hydrogen will be produced from the water, and if there are no easily oxidizable ions around the anode, oxygen will be produced from the water.

In Table VIII are listed several reactions which are typical of changes taking place during electrolysis. The electron is designated by  $e$ .

TABLE VIII  
TYPICAL ELECTROLYSIS REACTIONS

Electrolyte	Electrodes	Cathode Reaction	Anode Reaction
H <sub>2</sub> O	Platinum	$H^+ + e = \frac{1}{2}H_2$	$OH^- - e = \frac{1}{2}O_2 + \frac{1}{2}H_2O$
AgNO <sub>3</sub>	Silver	$Ag^+ + e = Ag$	$Ag - e = Ag^+$
AgNO <sub>3</sub>	Platinum	$Ag^+ + e = Ag$	$OH^- - e = \frac{1}{2}O_2 + \frac{1}{2}H_2O$
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Platinum	$Fe^{+++} + e = Fe^{++}$	$OH^- - e = \frac{1}{2}O_2 + \frac{1}{2}H_2O$
FeSO <sub>4</sub>	Platinum	$H^+ + e = \frac{1}{2}H_2$	$Fe^{++} - e = Fe^{+++}$
NaI	Platinum	$H^+ + e = \frac{1}{2}H_2$	$I^- - e = \frac{1}{2}I_2$
NaI	Silver	$H^+ + e = \frac{1}{2}H_2$	$I^- - e = AgI$
PbCl <sub>2</sub>	Platinum	$Pb^{++} + 2e = Pb$	$\begin{cases} Cl^- - e = \frac{1}{2}Cl_2 \\ OH^- - e = \frac{1}{2}O_2 + \frac{1}{2}H_2O \end{cases}$

If a platinum anode is surrounded by a solution of chloride ions in water, both Cl<sup>-</sup> ions and OH<sup>-</sup> ions will be colliding with the electrode and competing for the removal of the electron. Less energy is required to discharge the hydroxyl ion. Therefore when Cl<sup>-</sup> and OH<sup>-</sup> ions are in nearly the same concentration, practically pure oxygen will be evolved, but when the chloride ion is in large excess, chlorine gas will be produced at the anode. In 2 *M* hydrochloric acid, chlorine is evolved but in 0.02 *M* solution oxygen is evolved, whereas at intermediate concentrations a mixture of chlorine and oxygen is obtained. The products of electrolysis can be controlled not only by changing the concentration but also by changing the applied voltage.

**Decomposition Voltage.** When two platinum electrodes are placed in a solution of an electrolyte and a low voltage is applied, practically

no current flows through the circuit. As the voltage is gradually increased there may be a temporary flow of current until the products accumulate and produce an opposing voltage and cause the current to diminish. However, for each electrolyte there is a more or less definite voltage above which a steady current continues to flow. This voltage is called the *decomposition voltage*. At voltages above the decomposition voltage the current is proportional to the applied voltage. When the current flowing is plotted against the applied

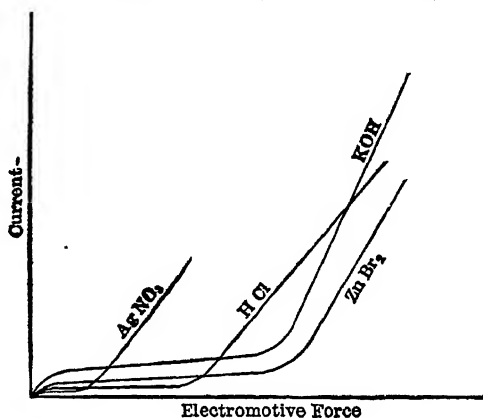


FIG. 118

voltage as shown in Fig. 118, the extrapolation of the steep line to cut the horizontal axis gives a measure of the decomposition voltage. In another method the applied voltage is increased until bubbles of gas or deposits of metal on an electrode can be detected with a microscope. Decomposition voltages vary with the conditions, but are characteristic of definite electrolytes. Thus the decomposition voltage of silver nitrate is 0.7, of lead nitrate is 1.8, and of zinc sulfate is 2.3 volts. It is a striking fact that most all strong acids and bases have decomposition potentials of 1.7 volts. They all behave alike in that at 1.7 volts or above they give off hydrogen and oxygen at the electrodes. Acids such as concentrated hydrochloric acid, which give products other than hydrogen and oxygen, have decomposition potentials which are below 1.7 volts.

Important use is made of decomposition potentials in the electrolytic separation of metals in a mixture of electrolytes. The electrolyte having the lowest decomposition potential will decompose first, and when the deposition of the metal is complete, the current will practically cease flowing; then if the applied voltage is raised above the decomposition potential of the second salt, the second metal will be

deposited. For example, in a mixture of cadmium, lead, and silver which is subjected to electrolysis, the decomposition potentials of the salts are as follows:  $\text{Cd}(\text{NO}_3)_2 = 2.0$  volts,  $\text{Pb}(\text{NO}_3)_2 = 1.5$  volts, and  $\text{AgNO}_3 = 0.7$  volt. If the applied electromotive force is made a little less than 1 volt all the silver will be deposited; then if the electromotive force is raised to about 1.6 volts, all the lead will be deposited; and finally, if the electromotive force is raised above 2 volts, the cadmium will be deposited.

If a solution of potassium sulfate is electrolyzed, hydrogen and oxygen are evolved because the hydrogen and hydroxyl ions are discharged at a lower voltage than the potassium ions and sulfate ions, as indicated by the normal electrode potentials. However, with very large current densities it is possible to deplete the hydrogen ions in the immediate neighborhood of the cathode to such an extent that some potassium will then deposit in a mercury cathode.

The deposition of metals can be altered by changing the solvent. Thus hydrogen is deposited at the cathode in an aqueous solution of sodium iodide, but sodium is deposited from a solution of sodium iodide in dry acetone.

The control of concentration as well as voltage is important in practical electroplating. In nickel plating, for example, if the acidity of the plating baths exceeds a certain limit, hydrogen will be liberated and the deposit will not be firm and smooth. The electroplating of a mixture of copper and zinc (brass) is another example. Ordinarily, when a mixture of zinc and copper salts is electrolyzed, copper is plated exclusively, because its decomposition potential is much less. However, the concentration of copper ions can be decreased enormously by adding potassium cyanide and locking up most of the copper in complex ions; under these conditions, when the zinc is very concentrated, both metals will be deposited together at the cathode.

Important changes in the electrodeposition of metals can be made through the use of rapidly rotating electrodes. When the solution in the neighborhood of the electrode is removed rapidly there is less chance for a change in concentration due to electrolysis. Smooth deposits can then be formed even with high current densities. If the solution is not agitated the current must often be kept so low as to require long times for deposition. Sometimes the introduction of a colloid like gelatine into the solution produces smaller crystals and a smoother deposit on the electrode.

**The Dropping-Mercury Electrode.\*** The decomposition voltages .

\*Kolthoff and Lingane, *Chem. Rev.*, **24**, 1 (1939); "Polarography," Inter Science Publishers, New York, 1941; O. H. Müller, *J. Chem. Education*, **18**, 65, 111, 172, 227 (1941).

obtained with a dropping-mercury electrode cathode are now often used for chemical analysis of inorganic and organic substances. Heyrovsky first developed a sensitive apparatus called the polarograph, which automatically records the current as the voltage is gradually increased. Each reducible substance has a definite characteristic decomposition potential and the voltage at which the current increases rapidly is used for qualitative analysis. Furthermore the magnitude of the current flowing at the decomposition voltage enables one to make an empirical calculation of the concentration of the material present which is undergoing reduction. The electrode surface is being continuously renewed as the mercury flows down from a small capillary, and the current passing across the boundary of the electrode depends on the rate at which the material in contact with the cathode can be reduced. This rate is proportional to the concentration of the material in the solution film surrounding the cathode. The concentration depends on the rate at which the material diffuses to the fresh film of the cathode surface and this in turn depends on the concentration in the body of the solution. There are other factors involved but simple, satisfactory analyses have been made on a great many different substances using empirical calibrations with known concentrations under conditions which are the same as those existing in the "unknown" solution.

**Polarization.** The production of a counter voltage by the products of electrolysis is called *polarization*. For example, if a current of electricity is passed through a solution of lead chloride between platinum electrodes, lead will be deposited on the cathode and chlorine on the anode. The lead-chlorine cell thus formed causes current to flow in the opposite direction and opposes the impressed voltage. Polarization may be caused also merely by the change in concentration around an electrode produced by the electrolysis. The polarization of an electrode can be determined by measuring the potential of the electrode against a reference electrode, such as a calomel electrode described on page 426, before and after the passage of the current. Polarization does not occur when all the reactions are rapid and the electrode is in a state of reversible equilibrium. The existence of polarization implies that one of the reaction steps involved is slow.

*Overvoltage* is a special case of polarization which depends on the evolution of gas. It is the difference between the decomposition voltage at which gas is evolved on an electrode and the voltage at which it is evolved under reversible conditions such as on a platinized platinum electrode. The overvoltage depends on the nature of the electrode, on the current density, and on other factors. The overvoltage for the liberation of hydrogen at a current density of 0.1 amp.



per sq. cm. are roughly as follows: platinized platinum 0.0; polished platinum 0.3; gold 0.6; iron 0.8; silver 0.9; nickel 1.02; zinc 1.1; lead 1.2; tin 1.2.

The decomposition potential must be at least as great as the equilibrium electrode potentials, given in the electromotive force series on page 438, plus the overvoltages. A high overvoltage leads to a higher decomposition potential. Many electroplating operations involve overvoltages. The high overvoltage of hydrogen on zinc accounts for the stability of a metal which might otherwise be expected to be more chemically active.

**Electrolytic Reduction and Oxidation.** Since hydrogen is liberated at the cathode in an atomic state at first, electrolysis provides a simple and effective means for hydrogenating materials. Electrolytic reduction depends on the supply of electrons produced at the cathode. Either hydrogenation or electrolysis or both may take place, depending on the conditions. Likewise oxidation may be produced electrolytically by removing electrons at the anode; and sometimes the oxygen liberated at the anode can be used to advantage. In some operations a porous cup is placed in the cell to keep the cathode and anode gases separated from each other. .

The current density, the cathode potential, the acidity of the solution, the overvoltage, and the nature of the electrode surface affect the electrolytic hydrogenation and reduction at the cathode.

The conversion of nitrobenzene into aniline is one of the classic examples of electrolytic hydrogenation. Not only can the reduction to aniline be accomplished effectively, but by suitable control of the potential and the acidity of the solution together with proper choice of electrodes it is possible to obtain large yields of any one of the intermediate products azoxybenzene, azobenzene, and hydrazobenzene, each representing a step in the reduction of nitrobenzene. Electrolytic oxidations at the anode are also important.

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## PROBLEMS

1. When filled with 0.02 molar potassium chloride solution, a certain conductance cell at 25° had a resistance of 95.1 ohms and when filled with 0.005 molar silver nitrate solution, it had a resistance of 414 ohms. What is the equivalent conductance of silver nitrate in 0.005 molar solution? *Ans.* 127 ohms<sup>-1</sup>.

2. Ten amperes of current flowed for 1 hour through water containing a little sulfuric acid. How many liters of gas were formed at 27° and 740° mm. pressure? *Ans.* 7.08 liters.

3. Determine the value of  $\Lambda_0$  for lithium chloride from the following data at 25°.

Equivalents per liter	0.05	0.01	.005	0.001	.0005
Equivalent conductance, $\Lambda$	100.1	107.3	109.4	112.4	113.5

*Ans.* 115.0.

4. MacInnes and Dole electrolyzed 1.0 *N* potassium chloride at 25° between a silver anode and a silver chloride cathode and found that 113.51 g. of water from the anode portion carried 7.9039 g. of potassium chloride. The anode reaction is  $\text{Ag} + \text{Cl}^- = \text{AgCl} + e$ ; the cathode reaction is  $\text{AgCl} + e = \text{Ag} + \text{Cl}^-$ . The middle portion, unchanged by the electrolysis, contained 7.1479 per cent by weight of potassium chloride. Calculate the number of equivalents of potassium ion which have migrated away from the solution surrounding the anode. The coulometer in the circuit gained 2.4835 g. of silver from the deposition of silver. Calculate the transference number of potassium in 1.0 *N* KCl. *Ans.* 0.4861.

5. A 0.02 molar solution of ammonium iodate has a specific conductance of 0.001962 reciprocal ohm. The transference numbers are  $n_c = 0.656$  and  $n_a = 0.344$ . What are the ionic conductivities of  $\text{NH}_4^+$  and  $\text{IO}_3^-$ ? *Ans.*  $\Lambda_{\text{NH}_4^+} = 64.3$ .  $\Lambda_{\text{IO}_3^-} = 33.7$ .

6. The equivalent conductance of an infinitely dilute solution of ammonium chloride is 149.7 and the ionic conductances of the ions,  $\text{OH}^-$  and  $\text{Cl}^-$ , are 198.0 and 76.3 respectively. Calculate the equivalent conductance of ammonium hydroxide at infinite dilution. *Ans.* 271.4.

7. At 25°, the equivalent conductance of sodium propionate at infinite dilution is 85.9. The ionic conductances of  $\text{Na}^+$  and  $\text{H}^+$  are 50.1 and 349.8 respectively. What is the equivalent conductance of an infinitely dilute solution of propionic acid at 25°? *Ans.* 385.6.

8. The following table gives the specific conductance of a solution of hydrochloric acid to 100 ml. of which have been added various amounts of a 7 *N* solution of sodium hydroxide. Neglecting the dilution effect of the small amount of hydroxide solution added, what is the normality of the hydrochloric acid solution?

NaOH, ml.	0.28	0.92	1.38	2.16
Conductance	0.0306	0.0166	0.0154	0.0288

*Ans.* 0.0804 *N*.

9. An electrolytic cell containing a cadmium sulfate solution was subjected to various applied potentials and the corresponding currents were measured. The results were as follows:

<i>E</i> (volts)	0.5	1.0	1.5	1.8	2.0	2.2	2.4	2.6	3.0
<i>I</i> (ampere)	0.002	0.004	0.006	0.007	0.008	0.028	0.069	0.110	0.192

What is the decomposition potential of cadmium sulfate? *Ans.* 2.06 volts.

10. If the specific conductance of 0.5 *M* boric acid ( $\text{H}_3\text{BO}_3$ ) solution is  $30.5 \times 10^{-6}$  mhos, what is (a) the specific resistance and (b) the equivalent conductance?

11. What is the molar conductance of mercury at 0°?

12. What is the specific conductance at 15° of a solution containing 0.1 gram of  $\text{CaSO}_4$  per liter? ( $\Lambda$  is practically equal to  $\Lambda_0$ .)

13. From the values of the equivalent conductance at different concentrations for aqueous nitric acid at 18°, determine the equivalent conductance of an infinitely dilute solution.

<i>Conc. (Milliequivalents per Liter)</i>	<i>Equivalent Conductance</i>
2.0	371.2
10.0	365.0
50.0	353.7
100.0	346.4

14. (a) How many ampere-hours of electricity are required to refine by electrolysis 453 g. (1 lb.) of copper, removing it from the impure anode and depositing it in a pure state on the cathode?

(b) If the potential drop across the electrolytic cell is 5 volts, how much will the electricity cost at 1 cent per kilowatt hour?

15. A solution of hydrochloric acid was electrolyzed in a transference cell between platinum electrodes. The cathode compartment contained 0.177 g. of chloride ions before the electrolysis and 0.163 g. after. A silver coulometer in series had a deposit of silver equivalent to 0.0825 g. of chloride ions. What are the transference numbers of  $\text{H}^+$  and  $\text{Cl}^-$ ?

16. A tube is partly filled with a very dilute solution of cupric chloride and a colorless solution placed on top so as to give a sharp colored boundary. A 50-volt potential is applied to the electrodes, which are 10 cm. apart. How long will it take the copper-ion boundary to move 5 cm. toward the cathode?

17. A glass tube having a uniform cross section of 1 sq. cm. was partly filled with 0.01 *N* hydrochloric acid and a solution of an inert electrolyte was flowed in on top of it so as to give a boundary. When a constant current of 10 milliamperes was passed through for 200 seconds, the hydrogen ions moved 17 mm. toward the cathode as shown by a color indicator for hydrogen ions. Calculate the transference number of the hydrogen ions in 0.01 *N* hydrochloric acid.

18. Calculate from the ionic conductances the equivalent conductance at 35° of  $\text{Na}_2\text{SO}_4$  at infinite dilution.

19. A 0.05 molar solution of cupric chloride has a specific conductance of 0.01149 reciprocal ohm. The transference numbers are  $n_c = 0.405$  and  $n_a = 0.595$ . What are the ionic conductivities of  $\text{Cu}^{++}$  and  $\text{Cl}^-$ ?

20. The following table gives the specific conductance of a solution of hydrochloric acid, to 100 ml. of which have been added various amounts of an 8 *N* solution of sodium hydroxide. Neglecting the dilution effect of the small amount of hydroxide solution added, what is the normality of the hydrochloric acid solution?

NaOH, ml.	0.32	0.92	1.56	2.34
Conductance, $\Lambda$	0.0322	0.0186	0.0164	0.0296

21. What are the probable products of electrolysis at each electrode when a current of electricity is passed through the following cells:

(a) An aqueous solution of copper sulfate with copper electrodes.

(b) An aqueous solution of ferrous sulfate with graphite electrodes.

- (c) An aqueous solution of lithium iodide with mercury electrodes.  
 (d) A solution of sodium iodide in acetone with platinum electrodes.

22. Determine the decomposition potential of copper sulfate from the following data:

$E$ (volts)	0.06	1.1	1.4	1.5	1.65	1.84
$I$ (ampere)	0.037	0.037	0.060	0.115	0.405	0.820

23. A long glass tube is provided with two electrodes of platinum wire at each end. When the tube is filled with 0.01  $N$  NaCl, the resistance is 200 ohms. Estimate with the help of a graphical interpolation how many grams of  $CaCl_2$  should be weighed out in a liter of solution so that the tube and solution will have a resistance of 5000 ohms.

24. A glass tube 4 cm. in diameter and 30 cm. long is closed at each end with a sheet silver electrode and filled with 0.01  $N$  silver nitrate. A voltage of 25 volts is applied. (a) How much current flows? (b) How many degrees will the temperature of the solution rise in 10 minutes assuming that the heat capacity of the solution is nearly 1 cal. per milliliter and that all the heat is taken up by the solution?

25. Estimate the specific conductance at 25° of water which contains fifty parts per million by weight of magnesium sulfate.

26. A 6-volt storage battery operates two 4-ampere lamps in parallel for 6 hours. How many grams of lead is oxidized? If 5 per cent of the energy goes into light and 95 per cent into heat, how many calories of heat are given off by the lamps?

27. The silver nitrate solution from the central compartment of a transference cell weighed 36.5 g. and was titrated with 32.7 ml. of ammonium thiocyanate solution, 1 ml. of which was equivalent to 0.0085 g. of silver nitrate. The solution from the cathode compartment weighed 43.17 g. and required 29.4 ml. of ammonium thiocyanate solution. A silver coulometer in series with the transference cell had a deposit of 0.0994 g. of silver. What are the transference numbers of the silver ion and the nitrate ion?

28. A current of 0.01 ampere is passed through an 0.01 molar solution of lithium chloride at 25° for 100 seconds using silver electrodes. (a) How much, if any, will each electrode gain in weight? (b) Estimate the number of equivalents of chloride ion which will be found in the 100 ml. of solution which surrounds the anode.

29. In 0.1  $N$   $Na_2SO_4$  the transference number of the sodium ion is 0.383. If a suitable boundary is made in a uniform glass tube 18 mm. in diameter, and 0.02 ampere is passed through the tube for 5 minutes, how far will the boundary of sodium ions move toward the cathode?

30. At 25° the equivalent conductance at infinite dilution  $\Lambda_0$  of sodium monochloroacetate is 89.8. Calculate  $\Lambda_0$  at 25° for monochloroacetic acid.

31. Calculate the equivalent conductance at infinite dilution of ammonium sulfate at 55°?

32. State quantitatively what the chemical changes will be at the cathode and the anode when a current of 1 ampere is passed for 10 minutes through the following solutions:

	(a)	(b)	(c)
Cathode	Graphite	Mercury	Silver
Solution	$H_2SO_4$	$ZnCl_2$	$FeCl_3$
Anode	Platinum	Zinc	Silver

33. The absolute velocities of ions have been determined by direct observation of a moving boundary. They may be calculated also from a knowledge of the equivalent conductance and the transference numbers. Imagine a solution containing  $c$  equivalents of a univalent electrolyte per 1000 ml. in a 1-cm. cube. Show that  $(v_c + v_a)(c/1000)F = I$  where  $v_c$  and  $v_a$  are the velocities of the ions and  $I$  is the current; and that since  $I = L$ , for a potential gradient of 1 volt per centimeter

$$\Lambda = (v_c + v_a)F$$

Using the transference numbers, calculate the absolute velocity of the  $K^+$  ion and the  $Cl^-$  ion at infinite dilution and  $25^\circ$ .

34. In determining the transference numbers of  $Ba(HSO_4)_2$  in concentrated  $H_2SO_4$  using platinum electrodes the following are the analyses for a typical measurement expressed in grams of  $BaSO_4$  per gram of solution:

Original	Anode compartment	Cathode compartment
0.02503	0.02411	0.02621

The solution had an average density of 1.90, the cathode compartment held 39 ml. and the anode compartment held 41 ml. During the experiment 4956 coulombs were transferred. What is the apparent transference number of  $Ba^{++}$  ion in the solution?

35. Outline methods by means of which the formation of a complex ion, such as  $Cu(CN)_2^-$ , might be determined in a solution containing both  $CuCl_2$  and  $KCN$ , using (a) conductance measurements, (b) measurements of transference numbers.

## CHAPTER XVI

### ELECTROMOTIVE FORCE

**Galvanic Cells.** The behavior of solutions during the passage of the electricity has been studied in the preceding chapters. Electrons are supplied to the cathode and removed from the anode by means of an external dynamo or battery, and the chemical changes are brought about by ions taking on electrons at the cathode and by ions losing electrons to the anode.

In the same way some chemical reactions produce an increase in the number of electrons at the surface of an electrode, thus making the electrode negative; and other reactions tend to remove electrons and make the electrode positive. The negative and positive electrodes produced in this way constitute an electrochemical cell. In the present chapter the relations between chemical reaction and the voltage of the electrodes will be studied quantitatively.

Since the year 1800, when Volta invented his electric pile, many different forms of galvanic cells have been introduced. One of the oldest and simplest cells is the Daniell cell, consisting of a zinc electrode immersed in zinc sulfate and a copper electrode immersed in copper sulfate, the two solutions being separated from each other by a porous cup. The electromotive force of such a cell is about 1 volt, the zinc electrode being negative and the copper positive.

The operation of the cell may be understood with the help of Fig. 119. Each electrode is bathed in a solution of its ions and there is an equilibrium at each as indicated by the reactions

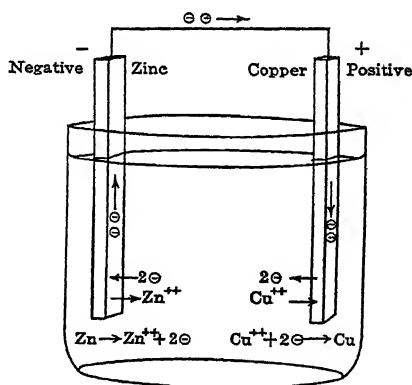
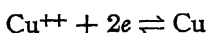
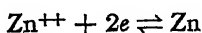


FIG. 119



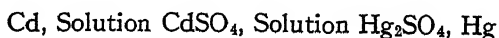
The copper ions, however, attract their valence electrons with greater force than do the zinc ions, i.e., copper is less easily ionized than zinc. In the competition for electrons, copper ions are more effective than zinc ions and they remove electrons from the copper electrode. When the wire between the two electrodes is disconnected the reactions stop, but as long as there is electrical connection between the two electrodes, electrons are removed from the copper electrode by the reaction  $\text{Cu}^{++} + 2e = \text{Cu}$  and electrons are provided at the zinc electrode by the reaction  $\text{Zn} \rightarrow \text{Zn}^{++} + 2e$ . Faraday's law applies and for each gram-equivalent of copper ions which is deposited from among the many ions which collide with the electrode, 1 gram-equivalent of zinc is ionized and 96,500 coulombs or  $6.02 \times 10^{23}$  electrons travel along the wire from the zinc to the copper-electrode.

As long as only a moderate current is drawn from the cell the original nature of the electrodes is not modified, the only change being the gradual depletion of the copper ions due to the separation of copper and their replacement by zinc ions. If the circuit is left open, the copper ions will diffuse throughout the whole cell and deposit on the zinc electrode. In this way, miniature local galvanic cells will be formed on the surface of the zinc, and the zinc will ionize continuously as though the main circuit were closed.

Unless chemically pure zinc is used, local action may occur, owing to the formation of local galvanic cells between the impurities in the electrode and the zinc. This action may be diminished by amalgamating the zinc electrode. In this process the mercury coats over the impurities. The saturated amalgam has the same potential as the pure zinc electrode. In the case of some metals a solid solution is formed which gives a slightly different potential.

Many other galvanic cells have been devised, but the zinc and copper cell serves to illustrate the general principle by which electricity can be furnished from chemical reactions. Several cells can be arranged in series to give a *battery* of higher voltage. Aside from the lead storage battery and the zinc-ammonium chloride dry battery these chemical sources of electricity are not widely used because the mechanical generation of electricity by dynamos is much cheaper. The measurement of voltage is important, however, in the solution of theoretical and laboratory problems.

**Standard Cells.** In making measurements of voltage the most widely used standard is the Weston or cadmium cell shown in **Fig. 120**. It is made up according to the scheme



A short platinum wire is sealed through the bottom of each limb of an H-shaped vessel. In one limb is placed a small amount of a 10 to 13 per cent cadmium amalgam, together with a layer of small crystals of  $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$ . In the other limb is placed a small amount of pure

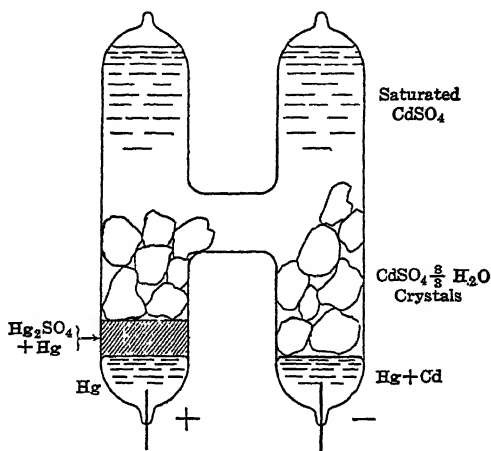


FIG. 120

mercury, over which is a layer of a paste, composed of solid mercurous sulfate and a saturated solution of cadmium sulfate. The cell is then filled with crystals of cadmium sulfate and a saturated solution of cadmium sulfate, and then sealed off. If carefully prepared with specially purified materials\* this cell will remain unaltered for years and will have an electromotive force, at  $20^\circ$ , of 1.0183 volts. Such cells are compared from time to time with standard cells of the same type calibrated at the National Bureau of Standards or other testing laboratory.

This cell is reversible, and unless abnormally large currents are drawn, the voltage remains constant. When it operates spontaneously, cadmium goes into solution as cadmium ions and the electrons left by this ionization pass around the wire to the positive electrode, where mercurous ions take them up and deposit as mercury atoms. When the cell is opposed by a larger electromotive force, the current flows in the opposite direction, cadmium is deposited, and mercury is dissolved. The solution is saturated with respect to both cadmium sulfate and mercurous sulfate, and a fixed concentration is maintained in spite of additions from the electrode or deposition on the electrode.

\* Wolf and Waters, *Bur. Standards Bull.*, 3, 623 (1907); 4, 1 (1907); Vosburgh and Derr, *J. Chem. Education*, 18, 87 (1941)



This condition of saturation is maintained no matter which way the current is flowing. The cadmium amalgam is solid, and its potential is independent of concentration between 10 and 13 per cent cadmium.

The effect of temperature on the Weston standard cell is small. It is given by the relation

$$\text{Electromotive force at } t^{\circ} = 1.0183 - 0.0000406(t - 20)$$

Weston cells in which the solution is unsaturated are often used because they have even smaller temperature coefficients.

**Reference Electrodes.** The electromotive force or voltage of a cell is equal to the sum of the potentials of its two half-cells.\* The *potential* of an electrode is the difference in potential between the electrode and the solution which bathes it. It is determined by combining it with a *reference electrode* which has an arbitrarily assigned potential and measuring the total voltage across the two half-cells. All electrode potentials are assigned on the assumption that the potential of the standard hydrogen electrode (described on page 448) is zero.

The calomel electrode shown at the left of Fig. 121 is a convenient reference electrode. It consists of pure mercury in the bottom of a vessel on which rests a paste of mercury and mercurous chloride (calomel). A solution of potassium chloride saturated with mercurous chloride makes electrical contact, through a side arm and a loosely fitting ground-glass joint, with any solution in which the electrode is placed. Such a connecting solution is called a *salt bridge*. Sometimes a beaker of potassium chloride solution is placed between the calomel electrode and the half-cell being measured, in order to minimize diffusion of mercurous ions into the solution. Electrical connection with the mercury is made through a platinum wire fused to a copper wire and sealed through a glass tube.

The electrode shown at the right of Fig. 121 is a *hydrogen electrode* which is arbitrarily assigned a value of 0.000 volt and used as the standard to which all other potentials are referred. Hydrogen gas at one atmosphere bubbles over a platinized platinum electrode immersed in a solution of hydrogen ions at an effective concentration or activity of 1 g. ion per 1000 g. of water. This standard hydrogen electrode will be discussed in more detail on page 448.

There are three different calomel electrodes. The most common is the normal calomel electrode which contains a molar solution of potassium chloride and has a voltage of +0.280 at 25° with reference to

\* There may be a small liquid junction potential also (page 459). The present discussion assumes that this effect has been eliminated or a correction applied.

the standard hydrogen electrode. The saturated calomel cell contains saturated potassium chloride and has a potential of  $+0.246$  with reference to the standard hydrogen electrode. The tenth normal calomel electrode is less frequently used. It is  $0.334$  volt more positive than the normal hydrogen electrode.

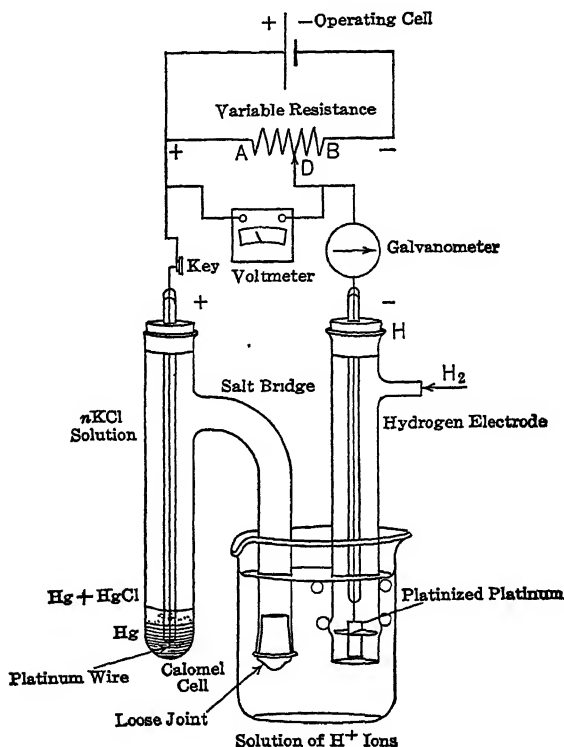


FIG. 121

Another useful reference electrode is the silver chloride electrode. An electrode of silver wire or a deposit of silver on a platinum wire is made the anode in a chloride solution and partly covered with a thin coating of silver chloride. The concentration of silver ions and chloride ions is fixed by the solubility of the silver chloride and maintained constant. The electrode is reversible with respect to both ions, i.e., the ions can be deposited on or produced from the electrode by reversing the current. This electrode is more difficult to prepare but it is valuable for certain measurements.

**The Measurement of Electromotive Force.** A simple voltmeter cannot be used alone for measuring the electromotive force of a small

cell because the operation of the voltmeter draws some current which causes chemical changes at the electrodes and produces a different voltage. Furthermore, if any appreciable current is drawn, the internal resistance of the cell is a complicating factor.

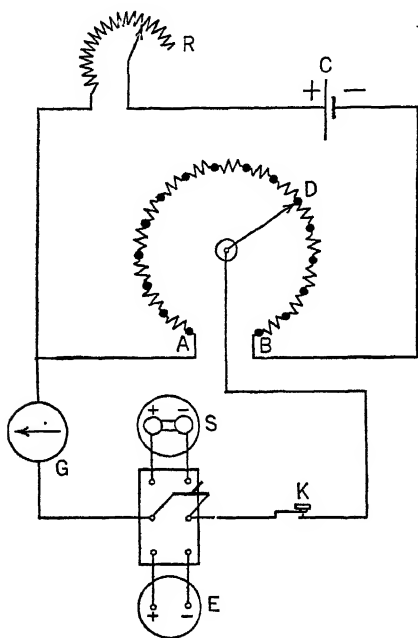
To avoid these difficulties the electromotive force is measured by balancing against the cell a known voltage under conditions such that practically no current flows. A simple and practical method for measuring the electromotive force of a cell is shown in Fig. 121. The

cell shown there consists of a hydrogen electrode and a calomel electrode. The two electrodes are connected to a variable, measured voltage through a galvanometer and key. The operating cell, of higher voltage than the cell to be measured, is connected to an adjustable rheostat  $AB$ . As the sliding contact is moved along the resistance a smaller fraction  $AD$  of the total potential drop is intercepted and the voltmeter connected across the resistance  $AD$  registers a lower voltage. The key is tapped momentarily as the sliding contact is moved until a position is found where the galvanometer is not deflected. At this position the voltage as read on the voltmeter is equal and opposite to that of the cell being measured.

FIG. 122

The cell is not altered by the taking of the measurement because practically no current flows through it.

More accurate measurements of electromotive force are made with a *potentiometer*, the principle of which is shown in Fig. 122. As in the arrangement shown in Fig. 121 a measured potential is balanced against the cell through a galvanometer. In the potentiometer the opposing potential is not read on a voltmeter but it is obtained accurately by connecting a known voltage across a uniform resistance  $AB$ . A sliding contact moves along the resistance and the ratio of  $AD$  to  $AB$  measures the fraction of the known potential drop which is picked off to oppose the electromotive force of the cell  $E$  being measured. The opposing potential is supplied by a working cell  $C$  connected



through an adjustable resistance  $R$  to the terminals of the uniform resistance  $AB$ . This resistance is divided into several equal parts and numbered. One of these small units of resistance is itself divided into 1000 parts (not shown in Fig. 122) so that the potential drop opposing the cell  $E$  can be adjusted to 0.0001 volt and less.

In practice the double-throw switch is connected to the standard cell  $S$  of known voltage, usually 1.0183 volt. The contacts are rotated to read 1.0183 and the key  $K$  is tapped momentarily as the external resistance  $R$  is adjusted, until the galvanometer  $G$  reads zero. When the voltage  $S$  is 1.0183 and the resistance is also 1.0183 units, it follows that each unit of the uniform resistance will read directly in volts. Then the switch is thrown to connect the potentiometer to a cell  $E$  the electromotive force of which is to be measured. The contact  $D$  is rotated to a position such that the galvanometer shows no deflection when the circuit is closed by the tapping key. Then the numbers on the potentiometer give directly in volts the electromotive force of the cell  $E$ .

**Reversible Cells.** Galvanic cells are either reversible or irreversible. Disregarding the slow process of diffusion, the Daniell cell may be taken as an example of a reversible cell. If an electromotive force slightly less than that of the cell is opposed to that of the cell, the current will still flow in the direction indicated in Fig. 119; but if the external electromotive force exceeds that of the cell, the current will flow in the opposite direction, and zinc will deposit and copper will dissolve. If an appreciable current is drawn from the cell, some of the electrical energy will be wasted as heat and the maximum work cannot be obtained. When only an infinitesimal current is consumed, the system is always practically in a state of equilibrium, and under these conditions the greatest possible electrical work is obtained. This maximum electrical work is definite and it is of great value in thermodynamical calculations. The measurements of irreversible cells are not significant in theoretical calculations but they may be of value in practical measurements. Sometimes it is possible to determine from the experimental behavior of a cell whether or not it is reversible. For example, if mechanical agitation produces marked unsteadiness in voltage or if the cell does not return to the same voltage after allowing a larger current to pass momentarily, the cell probably is not reversible.

The maximum electrical work done in the operation of a reversible galvanic cell can be calculated after measuring the voltage with a potentiometer and sensitive galvanometer in such a way that the only current consumed is that required to give a slight deflection of the galvanometer (perhaps one-millionth of an ampere).

**Relation between Chemical Energy and Electrical Energy.** When a cell operates reversibly at constant pressure and temperature, the electrical work obtained per gram-atom is  $nFE$ , where  $n$  is the valence change,  $F$  is the faraday or 96,500 coulombs, and  $E$  is the voltage or electromotive force of the cell. This maximum electrical work in joules may be converted into calories by dividing by 4.1833. Then  $F$  corresponds to 23,060 cal. per volt. In addition to the electrical work, some pressure-volume work may be done also, as, for example, when a gas is evolved by the operation of the cell. This pressure-volume work at constant pressure done on or by the atmosphere is not included in the free energy change  $\Delta F$ . Neither is it included in the maximum electrical work. Then

$$-\Delta F = nFE \quad [1]$$

According to this important equation, the electrical work done in a cell at constant temperature and pressure is equal to the decrease in free energy, whether or not there is a change in volume.

*Example 1.* The voltage of a copper-copper sulfate zinc sulfate-zinc cell is 1.10 volts. What is the free energy change involved when the cell consumes a mole of zinc?

$$\begin{aligned} \Delta F &= -nFE = 2 \times 96,500 \times 1.10 = -212,300 \text{ joules per mole} \\ &= -\frac{212,300}{4.1833} = -50,750 \text{ cal. per mole} \end{aligned}$$

The relation between the heat of reaction and the electromotive force of a cell may be obtained from the Gibbs-Helmholtz equation

$$\Delta F - \Delta H = T \left( \frac{\partial(\Delta F)}{\partial T} \right)_p \quad [2]$$

which was derived on page 143.

Substituting for  $\Delta F$  its equivalent,  $-nFE$ ,

$$\begin{aligned} -\Delta F &= nFE = -\Delta H + nFT \frac{\partial E}{\partial T} \\ -\Delta H &= nFE - nFT \frac{\partial E}{\partial T} \end{aligned} \quad [3]$$

This equation expresses the electromotive force of a reversible cell in terms of the temperature coefficient of the cell and the heat of the chemical reaction occurring within the cell. It may be used to calculate the heat of reaction from the measured voltage and the temperature coefficient of voltage. Since the precision of electrical measurements

is in general greater than that of thermal measurements, this indirect method often gives results which are more accurate than the calorimetrically determined values.

As discussed on page 98,  $\Delta H$  is the heat absorbed when the reaction takes place in a beaker or calorimeter at constant pressure and temperature. It is not the same as the heat absorbed when the same reaction takes place reversibly in the cell at constant pressure and temperature. Under these conditions the heat absorbed is  $T\Delta S$ , or

$$T\Delta S = \Delta H - \Delta F = nFT \frac{\partial E}{\partial T} \quad [4]$$

*Example 2.* Calculate the value of  $\Delta H$  for the reaction of the cadmium-silver chloride cell at  $25^\circ$  from the fact that the electromotive force is 0.67531 volt and the temperature coefficient is  $-0.000650$  volt per degree.

$$\begin{aligned} -\Delta H &= \frac{nF}{4.1833} \left( E - T \frac{\partial E}{\partial T} \right) = \frac{2 \times 96,500}{4.1833} (0.67531 + 298.1 \times 0.000650) \\ &= 40,080 \text{ cal.} \end{aligned}$$

The heat evolved as determined in a calorimeter is 39,530.

Further examples are given in Table I. The agreement between the calculated and the experimental values of  $\Delta H$  is entirely satisfactory.

TABLE I  
EXPERIMENTAL VERIFICATION OF THE GIBBS-HELMHOLTZ EQUATION

Cell	$E$ Volts	$\partial E / \partial T$ Volts/deg.	$-\Delta H$ equation (4)	$-\Delta H$ (obs.) calorimeter Cal.	$-\Delta F$ $\frac{nFE}{4.1833}$
Zn, $\text{ZnCl}_2(0.555m)$ , AgCl, Ag( $0^\circ$ )	1.015	$-0.000402$	51,990	52,050	46,830
Cd, $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ (satd.), AgCl, Ag( $25^\circ$ )	0.67531	$-0.00065$	40,080	39,530	31,160
Cd, $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ (satd.), $\text{PbCl}_2$ , Pb( $25^\circ$ )	0.18801	$-0.00048$	15,250	14,650	8,670
Pb, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ( $0.555m$ ), $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ (satd.), Cu( $0^\circ$ )	0.4764	$+0.000385$	16,900	17,530	21,990

A comparison of the last two columns is particularly interesting. The electrical energy in calories,  $nFE/4.1833$ , given in the last column, is the decrease in free energy which accompanies the reaction, and

it is a measure of the maximum useful work at constant pressure and temperature less the pressure-volume work.

Sometimes this maximum electrical work done is greater than  $-\Delta H$ , the ordinary heat of reaction, at constant pressure, and sometimes it is less. It is evident from equation (4) that if the temperature coefficient of the voltage is positive the maximum electrical work which can be done by the cell is greater than the heat which is evolved when the reaction takes place outside the cell (at constant pressure and temperature), and if the temperature coefficient has a negative sign the maximum electrical work is less.

For example, in the lead-copper cell  $-\Delta F = -\Delta H + 5,080$  cal. in agreement with a positive sign for the term  $nFT(\partial E/\partial T)$ .

In the special case where the voltage of the cell is independent of the temperature ( $\partial E/\partial T = 0$ ) the heat of reaction and the free energy change are equal.

**Classification of Cells.** Several different types of electrodes and cells which find uses in the study of electrochemistry are shown in the summary which follows. A semicolon indicates a contact between two different phases. The symbol Pt indicates an inert electrode like platinum.

#### TYPES OF ELECTRODES OR HALF-CELLS

Type	
1. Metal, metal ion	Cu; Cu <sup>++</sup>
2. Inert electrode, non-metal in solution, ion	Pt; I <sub>2</sub> (s), I <sup>-</sup>
3. Inert electrode, ions of different valence	Pt; Fe <sup>+++</sup> , Fe <sup>++</sup>
4. Inert electrode, gas, ion	Pt, H <sub>2</sub> ; H <sup>+</sup>
5. Inert electrode, neutral solutes in different states of oxidation	Pt; C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub> , C <sub>6</sub> H <sub>4</sub> O <sub>2</sub>
6. Amalgam electrode, ion	(Cd + Hg); Cd <sup>++</sup>
7. Electrode, insoluble salt or oxide, ion	Af, AgCl; Cl <sup>-</sup>

Any of these electrodes may be combined with any other to give a cell, the electromotive force of which is equal to the algebraic sum of the potentials of the two electrodes. If precipitation or chemical action occurs when the solutions surrounding the two electrodes are mixed, they must be kept separate with a salt bridge of potassium chloride or other suitable solution which permits the passage of an electric current.

When the electrodes are combined in such a way as to give a liquid junction, i.e., a contact between two different solutions, a small potential is created at such a liquid junction (page 459). It may be rendered nearly negligible by interposing a salt bridge of potassium

chloride. The presence or absence of such a liquid junction is important in handling problems of electrochemistry.

The cells may be classified as follows:

A. Cells with liquid junctions

1. Different electrodes       $\text{Zn}; \text{Zn}^{++}; \text{Cu}^{++}; \text{Cu}$
2. Concentration cells       $\text{Pt}, \text{H}_2; \text{HCl} (a = 1); \text{HCl} (a = 0.1); \text{H}_2, \text{Pt}$

The activities or effective concentrations of the electrolytes, expressed in gram-ions per 1000 g. of water, are given in parentheses.

B. Cells with the junction potential practically eliminated by means of a salt bridge, indicated by the sign  $||$ .

1. Different electrodes       $\text{Zn}; \text{Zn}^{++} || \text{Cu}^{++}; \text{Cu}$
2. Concentration cells       $\text{Pt}, \text{H}_2; \text{H}^+ (a = 0.1) || \text{H}^+ (a = 0.01); \text{H}_2, \text{Pt}$

Sometimes the junction potential is corrected by a calculation.

C. Cells without liquid junction

1. Different electrodes       $\text{Pt}, \text{H}_2; \text{H}^+, \text{Cl}^-; \text{Cl}_2, \text{Pt}$
2. Concentration cell of metal       $(\text{Hg} + 10\% \text{Cd}); \text{Cd}^{++}; (\text{Hg} + 1\% \text{Cd})$

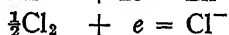
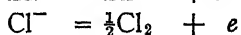
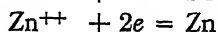
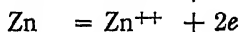
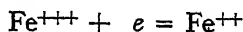
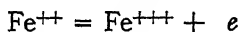
Cells with liquid junctions between *different* electrolytes cannot be given exact thermodynamic treatment and are to be avoided if possible. However, the cells in which the liquid junction potentials have been practically eliminated by a salt bridge are used widely in the determination of the activity of ions as, for example, in the case of hydrogen ions.

**Electrochemical Conventions.** The following statements are helpful in the study of electrochemical cells.

- |   |   |
|---|---|
| 1. <i>A substance is oxidized when it loses electrons</i> | <i>A substance is reduced when it gains electrons</i> |
|---|---|

The following are oxidations:

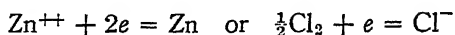
The following are reductions:



Ferrous ion with two electrons missing is oxidized to ferric ion by the loss of a third electron. The positive zinc ion is in the oxidized state, and the metal zinc is in the reduced state. The element chlorine is in the oxidized state and the chloride ion is in the reduced state.



2. *Standard electrode potentials are recorded in this book as reduction potentials.* Examples of the reactions producing the reduction potential are:



The standard  $\text{Zn}^{++}$ ;  $\text{Zn}$  electrode is recorded as having a negative sign. If the electrode is written in the opposite order,  $\text{Zn}$ ;  $\text{Zn}^{++}$ , it is given a positive sign, corresponding to an oxidation potential and to the oxidation reaction



3. *The electromotive force or voltage of a cell (emf) is the algebraic sum of the potentials of the two half-cells.*

In the cell  $A; A^+ || B^+; B$

$$E_{A; A^+} \quad E_{B^+, B}$$

$$E = E_{A; A^+} + E_{B^+, B} = -E_{A^+, A} + E_{B^+, B}$$

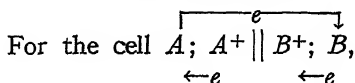
The sign and magnitude of  $E_{A^+, A}^0$  and  $E_{B^+, B}^0$  can be obtained from tables for the standard potentials at  $25^\circ$ , i.e., when the effective concentration is 1 gram-ion per 1000 g. of solvent.

4. *The potential of the standard hydrogen electrode* (1 atm. of hydrogen and 1 gram-ion of hydrogen ions per 1000 g. of water) *is taken arbitrarily as zero*, and all other potentials are defined by reference to it.

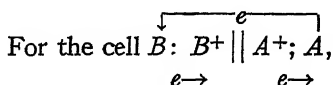
For the half-cell



5. *The electromotive force of a cell is arbitrarily given a positive sign if the electrode written at the left is negative, and the electrode at the right is positive.* Expressed in another way,  $E$  is positive (+) if electrons move from right to left within the cell.\* They must then move from left to right through the connecting wire.



$A$  is the negative electrode because electrons are given to it from solution;  $B$  is the positive electrode and for the whole cell  $E$  is positive (+).



$B$  is the positive electrode and  $E$  is negative (-).

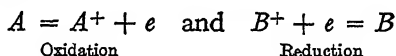
\* Some authors referring to the same convention speak of positive electricity moving from left to right within the cell.

In general, it is not known in advance which is the negative electrode, nor in which direction the chemical reaction of the cell will proceed spontaneously. By the conventions given here, however, one can determine whether or not the reaction is spontaneous *if* one determines which electrode is negative. Also one can specify which is the negative electrode when one knows whether or not the cell reaction is spontaneous. To make these correlations it is necessary to set up conventions which enable one to write the proper reaction corresponding to a given cell as written on paper. The order in which electrodes are written, left to right, determines the order in which the reaction is written. The reaction as written may be either spontaneous or non-spontaneous. To determine whether or not it is spontaneous experimental facts must be obtained.

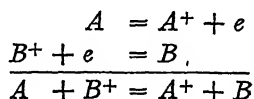
6. (a) *The "cell-reaction" taking place within the cell is always written arbitrarily so that oxidation occurs at the left electrode and reduction occurs at the electrode at the right (regardless of the sign of the electrodes).*

In the cell  $A; A^+ || B^+; B$

the half-cell reactions are

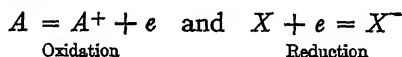


and the cell reaction is

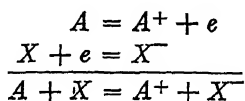


In the cell  $A; A^+ || X^-; X$

the half-cell reactions are

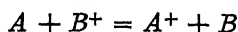


and the cell reaction is

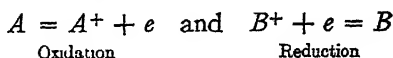


(b) *The cell corresponding to a given reaction is always written (regardless of sign) so that oxidation occurs at the left and reduction occurs at the right within the cell.*

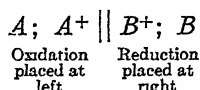
In the reaction



The total reaction may be split up into two parts, one substance being oxidized and the other being reduced



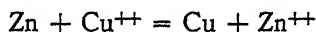
Then the cell is written



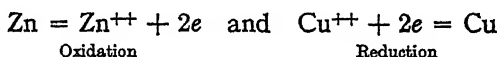
7. If for a given cell  $E$  is positive, i.e., the left electrode is negative,  $\Delta F$  is negative and the reaction is spontaneous. This relation follows from the facts that  $\Delta F = -nFE$  and that a reaction is spontaneous if  $\Delta F$  has a negative value.

Again, if the cell reaction as written is spontaneous, the left electrode of the corresponding cell as written on paper will be the negative electrode. It can be seen that  $E$  is a measure of the tendency for the cell reaction to proceed spontaneously in the conventional direction.

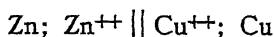
The reaction



can be split up into two parts, one an oxidation and the other a reduction.



The corresponding cell is



It is found in the laboratory by means of a potentiometer or by a litmus test (negative electrode gives blue) that the zinc electrode is negative. Then for the cell as written  $E = +$  and the reaction as written is spontaneous, i.e., zinc will displace copper ions from solution.

8. The reduced form of any metal or ion at unit concentration will reduce the oxidized form of another metal or ion at unit concentration which has a less negative standard electrode potential.

The magnitude of the negative potential is a measure of the ease with which an element or ion will lose electrons. Thus since,

$$E_{\text{Zn}^{++}; \text{Zn}}^0 = -0.761$$

and

$$E_{\text{Pb}^{++}, \text{Pb}}^0 = -0.126,$$

it follows that zinc with its more negative reduction potential will lose electrons more easily than lead. Therefore the reduced form of

zinc, metallic zinc, will give its electrons to the oxidized form of lead, lead ions; in other words, zinc reduces the lead ions to metallic lead and in so doing becomes oxidized to zinc ions.

Again  $\text{Fe}^{++}$  will reduce  $\text{Ag}^+$  to Ag because the standard reduction potential  $E^0$  of silver ion is less negative (or more positive) than the standard reduction potential of ferric ion:

$$E^0_{\text{Fe}^{+++}, \text{Fe}^{++}; \text{Pt}} = 0.783 \quad \text{and} \quad E^0_{\text{Ag}^+, \text{Ag}} = 0.799$$

**Standard Reduction Potentials.** The tendency of a metal to detach electrons and go into a given solution in the ionic form is measured by the single electrode potential of the electrode against a solution of its ions. Since this potential changes with the concentration of the ions it is necessary to adopt some standard concentration and the *standard electrode potential*  $E^0$  is defined as the potential of an element immersed in a solution of its ions at unit activity, i.e., effective concentration of 1 gram-ion per 1000 g. of solvent. This potential is referred to the standard hydrogen electrode potential as zero. The electrode must be reversible, of course, for thermodynamical calculations cannot be applied to irreversible electrodes.

The standard electrode reduction potentials of several elements referred to the standard hydrogen electrode are given in Table II. A negative sign indicates that the electrode is negative to a solution of the ions at unit activity when the electrode is connected to the standard hydrogen electrode.

This table includes the standard reduction potentials of ions as well as electrodes. Reducing ions tend to make an inert electrode more negative, and oxidizing ions tend to make it more positive. When ferrous ions,  $\text{Fe}^{++}$ , collide with a platinum wire, for example, they tend to give up electrons to the electrode and make it negative, while the ferrous ions themselves tend to become oxidized to ferric ions. Ferric ions,  $\text{Fe}^{+++}$ , on the other hand, tend to take electrons from the electrode to form ferrous ions and leave the electrode positively charged. The ratio of ferric to ferrous ions around an inert electrode determines the voltage. The standard reduction potential  $E^0$  for ions is taken as the potential of an inert electrode (platinum, for example, designated by "Pt") surrounded by a mixture of the reducing and oxidizing ions *each at unit activity* (or at the same activity). The potential is measured against the standard hydrogen electrode which is arbitrarily assigned a value of zero.

More often the calomel electrode is used for practical convenience and it is then necessary to add 0.2801 volt to the values thus obtained.

TABLE II

## STANDARD REDUCTION POTENTIALS

All ions are at unit activity, i.e., an *effective* concentration of 1 gram-ion per 1000 g. of water. Then the potential is designated by  $E^0$ .

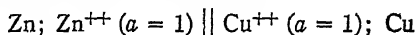
Electrode	$E^0$ in International Volts (Standard Hydrogen Electrode = 0)	Electrode Reaction
$\text{Li}^+; \text{Li}$	-3.0243	$\text{Li}^+ + e = \text{Li}$
$\text{K}^+; \text{K}$	-2.9239	$\text{K}^+ + e = \text{K}$
$\text{Na}^+; \text{Na}$	-2.7139	$\text{Na}^+ + e = \text{Na}$
$\text{Zn}^{++}; \text{Zn}$	-0.7611	$\text{Zn}^{++} + 2e = \text{Zn}$
$\text{Fe}^{++}; \text{Fe}$	-0.441	$\text{Fe}^{++} + 2e = \text{Fe}$
$\text{Cr}^{+++}; \text{Cr}^{++}; \text{Pt}$	-0.4000	$\text{Cr}^{+++} + e = \text{Cr}^{++}$
$\text{Cd}^{++}; \text{Cd}$	-0.4021	$\text{Cd}^{++} + 2e = \text{Cd}$
$\text{Tl}^+; \text{Tl}$	-0.3385	$\text{Tl}^+ + e = \text{Tl}$
$\text{Co}^{++}; \text{Co}$	-0.283	$\text{Co}^{++} + 2e = \text{Co}$
$\text{Ni}^{++}; \text{Ni}$	-0.236	$\text{Ni}^{++} + 2e = \text{Ni}$
$\text{I}^-; \text{AgI}(s); \text{Ag}$	-0.1522	$\text{AgI} + e = \text{Ag} + \text{I}^-$
$\text{Sn}^{++}; \text{Sn}$	-0.140	$\text{Sn}^{++} + 2e = \text{Sn}$
$\text{Pb}^{++}; \text{Pb}$	-0.126	$\text{Pb}^{++} + 2e = \text{Pb}$
$\text{H}^+; \text{H}_2, \text{Pt}$	0.0000	$\text{H}^+ + e = \frac{1}{2}\text{H}_2$
$\text{Ti}^{++++}; \text{Ti}^{+++}; \text{Pt}$	0.04	$\text{Ti}^{++++} + e = \text{Ti}^{+++}$
$\text{Sn}^{++++}; \text{Sn}^{++}; \text{Pt}$	0.13	$\text{Sn}^{++++} + 2e = \text{Sn}^{++}$
$\text{Cu}^{++}; \text{Cu}^+; \text{Pt}$	0.159	$\text{Cu}^{++} + e = \text{Cu}^+$
$\text{Cl}^-; \text{AgCl}(s); \text{Ag}$	0.2225	$\text{AgCl} + e = \text{Ag} + \text{Cl}^-$
Normal calomel electrode <sup>1</sup>	0.2801	$\frac{1}{2}\text{Hg}_2\text{Cl}_2 + e = \text{Hg} + \text{Cl}^-$
$\text{Cu}^{++}; \text{Cu}$	0.339	$\text{Cu}^{++} + 2e = \text{Cu}$
$\text{I}^-; \text{I}_2(s); \text{Pt}$	0.5350	$\frac{1}{2}\text{I}_2 + e = \text{I}^-$
$\text{H}^+; \text{quinhydrone}(s); \text{Pt}$	0.6994	$\text{C}_6\text{H}_4\text{O}_2 + 2\text{H}^+ + 2e = \text{C}_6\text{H}_6\text{O}_2$
$\text{Fe}^{+++}; \text{Fe}^{++}; \text{Pt}$	0.783	$\text{Fe}^{+++} + e = \text{Fe}^{++}$
$\text{Ag}^+; \text{Ag}$	0.799	$\text{Ag}^+ + e = \text{Ag}$
$\text{Hg}_2^{++}; \text{Hg}$	0.7986	$\text{Hg}_2^{++} + 2e = 2\text{Hg}^0$
$\text{Hg}^{++}; \text{Hg}_2^{++}; \text{Pt}$	0.906	$2\text{Hg}^{++} + 2e = \text{Hg}_2^{++}$
$\text{Br}^-; \text{Br}_2(l); \text{Pt}$	1.0651	$\frac{1}{2}\text{Br}_2(l) + e = \text{Br}^-$
$\text{Ti}^{+++}; \text{Ti}^+; \text{Pt}$	1.211	$\text{Ti}^{+++} + 2e = \text{Ti}^+$
$\text{Cl}^-; \text{Cl}_2(g); \text{Pt}$	1.3587	$\frac{1}{2}\text{Cl}_2(g) + e = \text{Cl}^-$
$\text{Pb}^{++}; \text{PbO}_2; \text{Pb}$	1.467	$\text{PbO}_2 + 4\text{H}^+ + 2e = \text{Pb}^{++} + 2\text{H}_2\text{O}$
$\text{Ce}^{++++}; \text{Ce}^{+++}; \text{Pt}$	1.609	$\text{Ce}^{++++} + e = \text{Ce}^{+++}$
$\text{Co}^{+++}; \text{Co}^{++}; \text{Pt}$	1.817	$\text{Co}^{+++} + e = \text{Co}^{++}$

<sup>1</sup> The concentration of KCl is by definition 1 mole per liter.

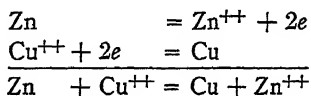
<sup>2</sup> There is evidence that the mercurous ion is doubled, giving not  $\text{Hg}^+$  but  $\frac{1}{2}\text{Hg}_2^{++}$ .

The values of  $E^0$  are obtained by making voltage measurements at several dilutions and extrapolating a function of the voltage to infinite dilution as explained on page 527. Considerable ingenuity and care are necessary in obtaining these values of  $E^0$ .

*Example 3.* Give the cell reaction and calculate the electromotive force, and the free energy change at 25° involved in the cell



The cell reaction is



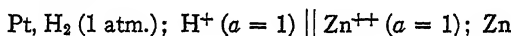
$$\begin{aligned} E^0 &= E^0_{\text{Zn}; \text{Zn}^{++}} + E^0_{\text{Cu}^{++}; \text{Cu}} = -E^0_{\text{Zn}^{++}; \text{Zn}} + E^0_{\text{Cu}^{++}; \text{Cu}} \\ &= -(-0.7611) + 0.339 \\ &= +1.1001 \end{aligned}$$

Because  $E$  has a positive value it can be stated that the left electrode is negative.

$$\begin{aligned} \Delta F^0 &= -E^0 n F = -1.1001 \times 2 \times 96,500 = -212,320 \text{ joules} \\ &= \frac{212,320}{4.1833} = -50,760 \text{ cal.} \end{aligned}$$

The reaction is spontaneous. Metallic zinc will reduce copper ion to copper.

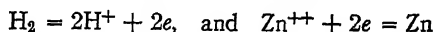
*Example 4.* In the cell



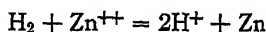
it is found with the help of a potentiometer that the zinc electrode is the negative electrode and that the voltage at 25° is 0.7611 volt. Calculate the standard reduction potential  $E^0_{\text{Zn}^{++}; \text{Zn}}$ . Since the negative electrode is at the right, the electrons move in the cell from left to right, hence the electromotive force of the cell is negative.

$$\begin{aligned} E^0 &= -0.7611 = E^0_{\text{Pt}, \text{H}_2; \text{H}^+} + E^0_{\text{Zn}^{++}; \text{Zn}} = 0 + E^0_{\text{Zn}^{++}; \text{Zn}} \\ E_{\text{Zn}^{++}; \text{Zn}} &= -0.7611 \end{aligned}$$

Write the cell reaction. The half-cell reactions are



and the cell reaction is

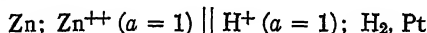


Calculate  $\Delta F^0$ .

$$\Delta F^0 = -E^0 n F = -(-0.7611 \times 2 \times 96,500 / 4.1833) = 35,114 \text{ cal}$$

The reaction is not spontaneous; hydrogen at atmospheric pressure will not reduce zinc ion to zinc when the effective concentration of hydrogen ion and of zinc ion is 1 gram-ion per 1000 g. of water.

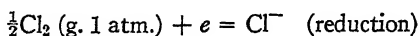
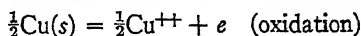
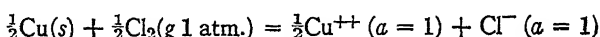
If the cell is written



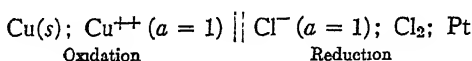
$E^0$  has a positive value instead of a negative one and  $\Delta F^0$  has a negative value; but the cell reaction is reversed. In other words it is concluded that zinc will

react spontaneously with hydrogen ion at unit activity. This conclusion is in complete harmony with the conclusion that hydrogen and zinc ion will not react.

*Example 5.* Write the cell which corresponds to the reaction



The cell is



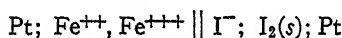
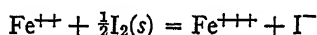
Calculate the voltage and the change in free energy of the reaction at 25°.

$$E = E^0_{\text{Cu}; \text{Cu}^{++}} + E^0_{\text{Cl}^-; \text{Cl}_2; \text{Pt}} = -(0.339) + 1.3587 = 1.0197 \text{ volts}$$

$$\Delta F^0 = -E^0 n F = -1.0197 \times 1 \times 96,500 / 4.1833 = -23,522$$

Copper and chlorine will react spontaneously to give cupric ions and chloride ions.

*Example 6.* Will ferrous ion reduce iodine to iodide ion at 25° according to the reaction



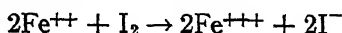
$$E^0 = E^0_{\text{Pt}; \text{Fe}^{++}, \text{Fe}^{+++}} + E^0_{\text{I}^-; \text{I}_2; \text{Pt}} = -0.783 + 0.5350 = -0.2480$$

$$\Delta F^0 = -E^0 n F = -(-0.2480 \times 1 \times 96,500 / 4.1833) = 5722 \text{ cal.}$$

The positive value of  $\Delta F^0$  (or negative value of  $E^0$ ) indicates that the reaction will not go spontaneously, i.e., solid iodine will not react with ferrous ion at unit activity to produce ferric ion at unit activity and iodide ion at unit activity.

The electromotive force of a cell is the sum of the potentials of the two electrodes or half-cells, and the free energy of a reaction is the sum of the free energies of the electrode reactions. Multiples of the reaction may be taken without changing the potential, but the free energy is changed owing to the factor  $n$  in the equation  $\Delta F = -nFE$ .

Thus for the reaction given in example 6



$$E = -0.2480 \quad \text{and} \quad \Delta F = 11,444 \text{ cal.}$$

The voltage is the same as for  $\text{Fe}^{++} + \frac{1}{2}\text{I}_2$  but the free energy change has doubled because the chemical reaction involves twice as much material.

**Chemical Equilibria and Electromotive Force.** It was shown on page 289 that in a reaction

$$\begin{aligned}
 aA + bB &= gG + hH \\
 \Delta F &= -RT \ln \frac{a_G^g \times a_H^h}{a_A^a \times a_B^b} + RT \ln \frac{a'_G{}^g \times a'_H{}^h}{a'_A{}^a \times a'_B{}^b} \\
 &= -RT \ln K + RT \ln Q
 \end{aligned} \tag{5}$$

where  $K$  represents the equilibrium constant involving the effective concentrations in a state of equilibrium, and  $Q$  represents the activity quotient, i.e., the ratio of the activities of the products to the activities of the reactants at any specified activities.

Remembering that according to equation (1)

$$\Delta F = -EnF$$

and substituting equation (1) into equation (5)

$$E = \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln Q \tag{6}$$

When the reaction is so planned that the reactants start at unit activity, i.e., the "effective" concentration is 1 gram-ion per 1000 g. of solvent and the final products are produced in concentrations such that their activities are unity, then  $\Delta F$  is written  $\Delta F^0$  and the last term becomes zero. Then equation (5) becomes

$$\Delta F^0 = -RT \ln K$$

Also, in this special case where all the reactants and products are at unit activity,  $E$  is defined as  $E^0$ . Then

$$E^0 = \frac{RT}{nF} \ln K \tag{7}$$

Substituting equation (7) into equation (6)

$$\begin{aligned}
 E &= E^0 - \frac{RT}{nF} \ln Q = E^0 - \frac{RT}{nF} \ln \frac{a'_G{}^g \times a'_H{}^h}{a'_A{}^a \times a'_B{}^b} \\
 &= E^0 - \frac{8.314 \times T \times 2.303}{n \times 96,500} \log Q
 \end{aligned} \tag{8}$$

When

$$T = 298.1$$

and

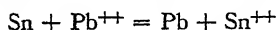
$$n = 1$$

$$E = E^0 - 0.0591 \log Q$$

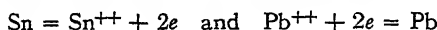


These equations are extremely important equations in the study of electrochemistry. Many special formulas concerned with theoretical and practical applications of electromotive force measurements follow directly from them. Equation (7) is used for calculations involving systems at equilibrium and the more general equation (8) is used for systems which are not in a state of equilibrium.

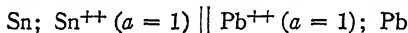
*Example 7.* Calculate from electromotive force data the equilibrium constant for the reaction between tin and lead and their ions at unit activity, thus



Splitting up the reaction into the two electrode reactions



and putting the oxidation reaction at the left in the corresponding cell at 25°



$$E^0 = E^0_{\text{Sn}; \text{Sn}^{++}} + E^0_{\text{Pb}^{++}, \text{Pb}} = -(-0.140) + (-0.126) = 0.014 \text{ volt}$$

$$E^0 = 0.014 \text{ and } \Delta F^0 = -nFE = -643 \text{ cal.}$$

$$E^0 = \frac{RT}{nF} \ln K = \frac{8.314 \times 298.1 \times 2.303}{2 \times 96,500} \log K = 0.0296 \log K$$

$$K = \frac{a_{\text{Sn}^{++}}}{a_{\text{Pb}^{++}}} = 2.97$$

In other words, when tin is added to a solution of lead salt, a state of equilibrium is reached in which the effective concentration of the tin ions is 2.97 times as great as that of lead ions.

In checking this equilibrium Noyes and Toabe added metallic tin to a solution of lead perchlorate at 25° and found at equilibrium 0.0716 mole of tin perchlorate and 0.0242 mole of lead perchlorate per liter. Assuming that the concentrations of tin perchlorate and lead perchlorate may be used in place of the activities

$$K = \frac{a_{\text{Sn}^{++}}}{a_{\text{Pb}^{++}}} = \frac{0.0716}{0.0242} = 2.96$$

In order to approach the equilibrium from both sides they also added lead to a solution of tin perchlorate, and found at equilibrium 0.0704 mole of tin perchlorate and 0.0233 mole of lead perchlorate per liter.

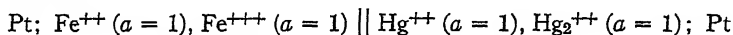
$$K = \frac{a_{\text{Sn}^{++}}}{a_{\text{Pb}^{++}}} = \frac{0.0704}{0.0233} = 3.02$$

Carrying out a similar calculation for the addition of zinc to copper ions it is found that  $E^0 = 1.1001$  and  $\frac{a_{\text{Zn}^{++}}}{a_{\text{Cu}^{++}}} = 10^{37}$ . In other words, the removal of copper ions by zinc is practically complete.

Referring to Table II, any electrolyte in the reduced or "ous" state (at unit activity) will tend to reduce any electrolyte in the oxidized or "ic" state (at unit activity) which is lower in the table. Any combination of electrodes may be made and from the corresponding voltage the equilibrium constant may be calculated. Moreover, the ratio of concentrations when equilibrium is attained can be calculated.

*Example 8.* To what extent will mercuric ion be reduced by the addition of ferrous ion at 25°?

The cell is



$$\begin{aligned} E^0 &= E^0_{\text{Pt}(\text{Fe}^{++}, \text{Fe}^{+++})} + E^0_{(\text{Hg}^{++}, \text{Hg}_2^{++}) \text{Pt}} \\ &= -0.783 + 0.906 = 0.123 \end{aligned}$$

The cell reaction is

$$\begin{aligned} \text{Fe}^{++} + \text{Hg}_2^{++} &= \text{Fe}^{+++} + \frac{1}{2} \text{Hg}_2^{++} \\ E^0 = 0.123 &= \frac{8.314 \times 298.1 \times 2.303}{1 \times 96,500} \log K \\ K &= \frac{a_{\text{Fe}^{+++}} \times a_{\text{Hg}_2^{++}}^{1/2}}{a_{\text{Fe}^{++}} \times a_{\text{Hg}^{++}}} = \text{antilog } 2.081 = 121 \end{aligned}$$

This calculation shows that the ferrous ion reduces the mercuric ion to such an extent that, at equilibrium, the product of the activity of the ferric ion by the square root of the activity of the mercurous ion ( $\text{Hg}_2^{++}$ ) is 121 times as great as the product of the activities of the ferrous and mercuric ions.

These examples have served to illustrate equation (7) which gives the relation between the equilibrium constant and the standard electrode potentials. The more general equation (8) which shows the relation between  $E$ ,  $E^0$ , and  $Q$ , will now be applied. It can be used to calculate the voltage of a cell when the ions are not at unit activity and it can be used to calculate the effective concentration of ions from the electromotive force of the cell.

*Example 9.* Calculate the potential of the following cell at 25°.



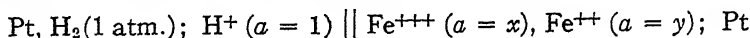
The cell reaction is

$$\begin{aligned} \text{Sn} + \text{Pb}^{++} &= \text{Sn}^{++} + \text{Pb} \\ E &= E^0 - \frac{RT}{nF} \ln Q = 0.0140 - \frac{0.0591}{2} \log \frac{0.6}{0.3} \\ &= 0.0140 - 0.0089 = 0.0051 \text{ volt} \end{aligned}$$

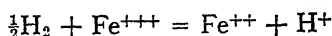
$$\Delta F = -EnF = -0.0051 \times 2 \times 96,500 / 4.1833 = -235 \text{ cal.}$$

The free energy decrease  $\Delta F$  for this reaction is less than  $\Delta F^0$  for the reaction where both reactants and products are at unit activity (example 7) because here the specified activity of the products is greater than the specified activity of the reactants. The activities 0.3 and 0.6 are arbitrarily assigned and are not to be confused with the equilibrium concentrations.

The validity of equation (8) may be illustrated by determining the voltage of the ferric-ferrous electrode using the cell



The cell reaction is



Applying equation (8)

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{H}^+} \times a_{\text{Fe}^{++}}}{a_{\frac{1}{2}\text{H}_2} \times a_{\text{Fe}^{+++}}}$$

but since  $a_{\text{H}^+} = 1$  and  $a_{\text{H}_2} = 1$ ,

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{Fe}^{++}}}{a_{\text{Fe}^{+++}}} \quad [9]$$

$E^0$  is the electromotive force of an inert electrode surrounded by equal activities of ferrous and ferric ions when measured against the normal hydrogen electrode, for when  $a_{\text{Fe}^{++}}$  and  $a_{\text{Fe}^{+++}}$  are equal, the last term becomes zero.

$E^0$ , as calculated from the following data of Peters,\* is reasonably constant even though the ratios are the ratios of concentrations rather than activities.

TABLE III

CHANGE OF VOLTAGE WITH CHANGE IN RATIO OF OXIDIZING TO REDUCING IONS

$c_{\text{Fe}^{+++}}/c_{\text{Fe}^{++}}$	0.5/99.5	2/98	10/90	30/70	50/50	80/20
$E$	0.580	0.615	0.655	0.690	0.713	0.747
$E^0$	0.712	0.712	0.710	0.711	0.713	0.712

The absolute values of  $E^0$  are only approximate because no attempt was made to obtain activities or effective concentrations. The solutions were made tenth-normal with respect to hydrochloric acid to prevent hydrolysis.

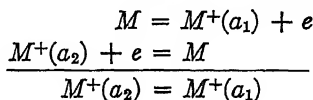
\* Peters, *Z. physik. Chem.*, **26**, 193 (1898).

Popoff and Kunz have investigated this system more fully, extrapolating to zero concentration of iron ions and zero concentration of hydrochloric acid. They obtained a series of values of  $E^0$  in progressively more dilute solutions of ferrous and ferric chloride and extrapolated to infinite dilution of iron chlorides. This extrapolated value of  $E^0$  in  $N/10$  hydrochloric acid is 0.731, and it may be considered an accurate value obtained with activities instead of concentrations. There is a complication, however, in that the hydrochloric acid changes the character of the solution and affects the value of  $E^0$ . A value of 0.747 for  $E^0$  in pure water was obtained by determining the extrapolated value of  $E^0$  in solutions of different normality with respect to hydrochloric acid and extrapolating these values to zero concentration of hydrochloric acid. The value is somewhat in doubt on account of hydrolysis. Schumb and Sweetzer\* obtained a value of 0.783 by measuring the equilibrium between silver and ferric perchlorate.

**Concentration Cells.** When two electrodes of the same material are immersed in solutions of their ions at the same concentration, there will be no difference of potential. If, however, the two solutions are of different concentrations the cell will exhibit a definite electromotive force which depends on the ratio of the activities of the ions in the two solutions. Such a cell is represented by the arrangement shown in (10).



Writing the cell reaction in such a way that the left electrode is oxidized and the electrode at the right is reduced



The mathematical formulation of this cell is particularly simple because the reactants and the products are the same. Referring back to the fundamental formula (8), placing the products in the numerator as usual, neglecting solids because the activities of solids are taken as unity, and considering only the activities of the  $M^+$  ion,

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_1}{a_2}$$

But  $E^0 = \frac{RT}{nF} \ln K$ , and for this case  $K = 1$  because equilibrium is established only when  $a_1 = a_2$ .

\* Schumb and Sweetzer, *J. Am. Chem. Soc.*, **57**, 871 (1935).

Then  $E^0 = 0$ , and

$$E = - \frac{RT}{nF} \ln \frac{a_1}{a_2} \quad [11]$$

If, for example, the concentrations of the univalent metal ions are such that  $a_1 = 0.01$  and  $a_2 = 0.1$ , the potential of the concentration cell at  $25^\circ$  is  $-\frac{8.314 \times 298.1 \times 2.303}{96,500} \times \log \frac{0.01}{0.1}$  or  $+0.059$  volt. The positive value of  $E$  shows that the reaction is spontaneous; i.e., there is a tendency for ions at  $0.1$  ( $a_2$ ) to diffuse into the more dilute solution where  $a_1 = 0.01$ . It is obvious from an inspection of the cell that the electrode immersed in the  $0.1$  solution of positive ions will be positive with reference to the more dilute solution, because there are more collisions of positive ions per second per square centimeter on the surface of the electrode.

If in the cell just given the more concentrated solution is placed at the left (i.e.,  $a_1 = 0.1$  and  $a_2 = 0.01$ ), the left electrode will be positive and electrons will be moving from left to right within the cell. The voltage  $E$  of the cell will then have a negative sign. In agreement with equation (11),  $\log \frac{a_1}{a_2}$  becomes positive (i.e.,  $\log \frac{0.1}{0.01}$ ), and  $E$  has a negative value. Then  $\Delta F$  has a positive value. According to this calculation the diffusion of  $M^+$  ion from a solution in which  $a = 0.01$  to one in which  $a = 0.1$  is *not* a spontaneous process.

In dilute solutions the following equation may be used as an approximate form of equation (11) for positive ions where  $c_1$  is the concentration at the left electrode and  $c_2$  is the concentration at the right.

$$E = - \frac{RT}{nF} \ln \frac{c_1}{c_2} \quad [12]$$

If the cell is made with negative ions,  $M^-$ , such as iodide ions, the arrangement is



the cell reaction is

$$M^-(a_1) = M^-(a_2)$$

and the formula for the voltage of the concentration cell with negative ions is

$$E = - \frac{RT}{nF} \ln \frac{a_2}{a_1} \quad [13]$$

Also as an approximate formula

$$E = - \frac{RT}{nF} \ln \frac{c_2}{c_1} \quad [14]$$

Another type of concentration cell is shown as follows:



The cell reaction is  $M(a_1) = M(a_2)$  and the formula for the electromotive force is

$$E = - \frac{RT}{nF} \ln \frac{a_2}{a_1} \quad [15]$$

where  $a_1$  and  $a_2$  refer to the concentration of the metal at the left electrode and at the right electrode respectively. A metal dissolved in mercury may be used to illustrate this type. In Table IV are recorded voltages of various pairs of zinc amalgams together with the values calculated by equation (15).

TABLE IV  
ELECTROMOTIVE FORCE OF ZINC AMALGAMS<sup>1</sup>

<i>T</i> , degrees	<i>c</i> <sub>1</sub>	<i>c</i> <sub>2</sub>	<i>E</i> (obsd.)	<i>E</i> (calcd.)
284.6	0.003366	0.00011305	0.0419	0.0416
291.0	0.003366	0.00011305	0.0433	0.0425
285.4	0.002280	0.0000608	0.0474	0.0475
333.0	0.002280	0.0000608	0.0520	0.0519

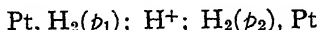
<sup>1</sup> Meyer, *Z. physik. Chem.*, **7**, 477 (1891).

The agreement between the observed and calculated values of  $E$  is good even when concentrations are substituted for activities. That the above formula holds for zinc amalgams may be considered as a proof that zinc dissolves in the mercury as monatomic molecules. Thus, if the zinc were present in the mercury in the form of diatomic molecules, the electrical energy would be equal to  $2FE$  per gram-ion and the value of the electromotive force would be just one-half the above calculated value. The mercury in the amalgam has been shown to exert no effect upon the electromotive force of the cell, so long as the dissolved metal has a more negative potential than has the mercury.

In concentrated amalgams, however,\* some of the dissolved metal combines with the mercury, not all is available for direct ionization, and the concentrations cannot be substituted for the activities.

\* Richards and Daniels, *J. Am. Chem. Soc.*, **41**, 1732 (1919).

Similar concentration cells can be arranged in which the electrodes are gas electrodes at different partial pressures,  $p_2$  and  $p_1$ . The activities of the electrodes are proportional to the partial pressures of the gas, thus



and

$$E = - \frac{RT}{nF} \ln \frac{p_2}{p_1}$$

*Example 10.* Two hydrogen electrodes are set in a solution of hydrochloric acid at 25°. The pressure of hydrogen over one is 1 atm. but in the other the hydrogen is mixed with nitrogen so as to give a partial pressure of hydrogen of 0.5 atm. Which will be the positive electrode and what will be the voltage of the cell?

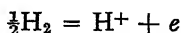
The hydrogen under the higher pressure will give more hydrogen ions, leaving it the negative electrode. If the electrode bathed with hydrogen at the higher pressure is placed at the left in the cell just given

$$E = - \frac{RT}{nF} \ln \frac{p_2}{p_1} = - \frac{8.314 \times 298.1 \times 2.303}{2 \times 96,500} \log \frac{0.5}{1}$$

$$= 0.0089 \text{ volt}$$

**The Hydrogen Electrode.** The determination of the effective concentration of hydrogen ions in a solution has been of great practical importance, and the hydrogen electrode was the first and most important means of making these determinations.

Hydrogen gas does not conduct the electric current, and it cannot be used alone as an electrode, but when adsorbed on the surface of platinum it behaves just as if it were a metallic electrode and the reaction



is completely reversible as shown by laboratory tests and by thermodynamic criteria. Hydrogen ions apparently can break away from the layer of hydrogen atoms adsorbed on the surface; and the platinum acts as an inert electrical conductor without entering the reaction of the cell. To act efficiently the electrode must be covered with platinum black to give a large surface area for adsorption. The electrode is arranged in such a way that hydrogen bubbles up around the platinum, or else the electrode is partly immersed in the solution and partly in the hydrogen. The level of the liquid is changed as the gas bubbles out from a glass hood which surrounds the electrode, and thus the electrode is bathed alternately with hydrogen and with the solution.

Numerous forms of hydrogen electrodes have been devised but the general form already shown in Fig. 121 is satisfactory. In accurate

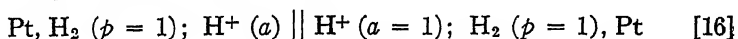
work the hydrogen must be at a definite, known pressure and it must contain no oxygen. Corrections may be made for the vapor pressure of water. Several solutes may interfere with the proper operation of the hydrogen electrode, particularly oxidizing agents or platinum poisons. Any oxidizing substance or unsaturated compound which will be acted on by hydrogen in the presence of platinum must be avoided. This includes nitrate ion, ferric ion, chromates, and organic oxidizing agents. Poisons include traces of arsenic and sulfur compounds. In some solutions it is not feasible to bubble gas through the cell because the equilibrium of the solution with other gases is upset as, for example, in the blood. In such a case the cell is closed with hydrogen above the solution and shaken thoroughly.

Chlorine and some other gases may be used with platinum as gas electrodes for determining chlorides or other ions. Some gas electrodes as, for example, the oxygen electrode, are useful in titrations, but they are of little theoretical interest because they are irreversible. With these electrodes it is not possible to calculate the activities of the ions from a given emf., but end points may be determined in titrations.

The hydrogen electrode is used to determine the activity or effective concentration of hydrogen ions with the help of a formula similar to equation (11) for the electromotive force of a concentration cell.

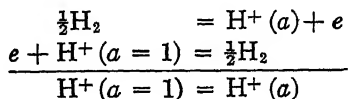
Hydrogen electrodes with hydrogen at 1 atm. pressure are placed in the solutions of different hydrogen-ion concentrations.

Making one of the activities unity, the other may be calculated in a very simple manner using the cell



Usually  $a_{\text{H}^+}$  will be less than 1, making the electrode at the left the negative electrode.

The cell reaction is



According to equation (8)

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{H}^+}}{1}$$

When both activities are unity in a concentration cell according to equation (7)

$$E^0 = \frac{RT}{nF} \ln K = \frac{RT}{nF} \ln 1 = 0$$



Then

$$E = -\frac{RT}{nF} \ln \frac{a_{H^+}}{1} = -\frac{RT}{nF} \ln a_{H^+} \quad [17]$$

In practice it is much easier to use a normal calomel cell in place of a standard hydrogen electrode.

Careful measurements have shown that the normal calomel electrode is positive with respect to the standard hydrogen electrode by 0.2801 volt at 25°. It is, of course, still more positive to a hydrogen electrode placed in solution having hydrogen-ion activities less than unity.

The formula for the hydrogen electrode against a normal calomel electrode at 25° is

$$E = -0.0591 \log a_{H^+} + 0.2801 = 0.0591 \log \frac{1}{a_{H^+}} + 0.2801 \quad [18]$$

This is the working equation for the hydrogen electrode using hydrogen at 1 atm., a normal calomel electrode, and a salt bridge of potassium chloride which reduces the liquid junction potential to a minimum. It must be realized that the effective concentrations or activities of hydrogen ions are given by this formula, but in the very dilute solutions which are usually studied the actual concentrations are practically the same. There is an uncertainty regarding the junction potential which prevents the accurate determination of absolute values of individual ion activities. No matter what the theoretical background is, the practical value of the hydrogen electrode has been abundantly established. The voltage measurements obtained from hydrogen electrodes are correlated, quantitatively, with a wide variety of chemical and biological phenomena.

**Hydrogen-Ion Concentrations.** Hydrogen-ion activities are commonly expressed in terms of *pH* rather than in terms of effective concentration  $a_{H^+}$ . The relation of *pH* to effective hydrogen-ion concentration, expressed by the symbol  $a_{H^+}$ , is indicated by the relation,

$$pH = \log \frac{1}{a_{H^+}} \quad \text{or} \quad a_{H^+} = 10^{-pH} \quad [19]$$

The term *pH* was first proposed for biochemical studies by Sørensen in 1909.

*Example 11.* What is the effective concentration of hydrogen ions, in a solution which has a *pH* of 3?

$$a_{H^+} = 10^{-pH} = 10^{-3} = 0.001 \text{ gram-ion per 1000 g. H}_2\text{O}$$

What is the  $pH$  of a solution which is 0.0002 molal in hydrogen ions?

$$pH = \log \frac{1}{a_{H^+}} = \log \frac{1}{2 \times 10^{-4}} = \log 5 \times 10^3 = 3.699^*$$

Equation (18) may be rewritten to give

$$pH = \frac{E - 0.2801}{0.0591} \quad [20]$$

The approximate value of the ionic product of water,  $C_{OH^-} \times C_{H^+}$ , at 25° is  $1 \times 10^{-14}$ .† If the normal concentration of hydroxyl ions in water is increased by the addition of a base, the concentration of hydrogen ions is decreased. Thus, if in the aqueous solution of a base the activity of the hydroxyl ions is  $1 \times 10^{-4}$  the activity of the hydrogen ions must be  $10^{-14}/10^{-4} = 10^{-10}$  and the  $pH$  is 10. In other words,

$$pH + pOH = 10 + 4 = 14 \quad [21]$$

A few illustrations of the relation between concentration  $a_{H^+}$  and  $pH$  are given in Table V.

TABLE V  
 $a_{H^+}$  AND  $pH$  VALUES OF COMMON ACIDS AND BASES

Solute	Concentration Moles per Liter	$a_{H^+}$	$pH$
HCl	1.00 <i>M</i>	$8.0 \times 10^{-1}$	0.10
HCl	0.10 <i>M</i>	$8.4 \times 10^{-2}$	1.07
HCl	0.01 <i>M</i>	$9.5 \times 10^{-3}$	2.02
NaOH	1.00 <i>M</i>	$0.90 \times 10^{-14}$	14.05
NaOH	0.10 <i>M</i>	$0.86 \times 10^{-13}$	13.07
NaOH	0.01 <i>M</i>	$0.76 \times 10^{-12}$	12.12
CH <sub>3</sub> COOH	0.10 <i>M</i>	$1.36 \times 10^{-3}$	2.87
NH <sub>4</sub> OH	0.10 <i>M</i>	$5.4 \times 10^{-12}$	11.27

Another term related to  $pH$  is now often used. Just as  $pH = -\log a_{H^+}$ , so  $pK$  is a symbol which stands for  $-\log K$  where  $K$  is the ionization constant of a weak acid.

**Titration with the Hydrogen Electrode.** Since the neutralization of acids and bases is accompanied by changes in the concentration of

\* The calculation may also be made as follows:  $pH = -\log a_{H^+} = -\log (2 \times 10^{-4}) = -(\bar{4} + 0.301) = 3.699$ . Further examples of negative logarithms of this type are given in "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., New York, 1928, p. 11.

† Complete calculations are given on page 481.

hydrogen and hydroxyl ions, it is apparent that the hydrogen electrode can be employed in place of an indicator in titrations. The first application of the hydrogen electrode to the titration of acids and bases was made by Böttger,\* who showed that the method was applicable to titrations where ordinary indicators fail to give satisfactory results as, for example, in the titration of deeply colored or turbid solutions.

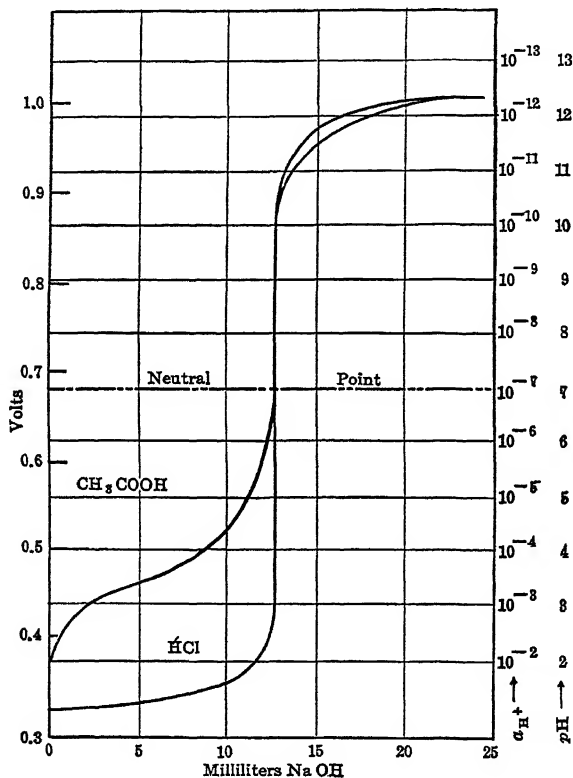


FIG. 123

The simple apparatus shown in Fig. 121 may be used for such a titration.† The results of the titration of hydrochloric and acetic acids by sodium hydroxide are shown graphically in Fig. 123, where the abscissas represent the number of milliliters of sodium hydroxide added to the solution from a buret, and the ordinates represent the corresponding values of the electromotive force. The scale of hy-

\* Böttger, *Z. physik. Chem.*, **24**, 253 (1897).

† Hildebrand, *J. Am. Chem. Soc.*, **35**, 847 (1913).

drogen-ion concentrations and  $pH$  at the right of the diagram is calculated by means of equations (18) and (20). It will be seen that, in both acids, a sharp rise occurs in the curves when the end point of the titration is reached.

When the solution is exactly neutral the activities of the hydrogen ions and hydroxyl ions are the same and equal to  $10^{-7}$  at  $25^\circ$ . The voltage of the hydrogen electrode against the calomel electrode then is

$$E = 0.0591 \log \frac{1}{1 \times 10^{-7}} + 0.280 = 0.694 \text{ volt}$$

At the end point the concentration of hydrogen ions is very small and the number of hydrogen ions in a drop of acid, or of hydroxyl ions in a drop of alkali, is large in comparison. A slight addition of either acid or alkali then makes a large change in the hydrogen-ion activity. Regarding the solutions before and after the addition of alkali as the two solutions of a concentration cell, it is seen that the voltage change must be large when the ratio  $a_1/a_2$  of equation (11) is large. Near the end point, then, a milliliter will give a much greater change in voltage and a steeper curve. When the solution is already strongly acid or strongly alkaline, the addition of a few more hydrogen or hydroxyl ions from a buret has only a slight effect and the curve is flat.

Acetic acid shows an initial electromotive force greater than that of hydrochloric acid, because it is slightly dissociated and the hydrogen-ion concentration at a given concentration of acid is much less. It should be noticed that the first additions of alkali cause a marked decrease in acidity. The alkali not only neutralizes the acid and thereby converts hydrogen ions into water but it also produces sodium acetate which is largely dissociated. This large increase in acetate ions causes the repression of ionization of the acetic acid and in turn causes more hydrogen ions to change into undissociated acetic acid molecules (page 479).

Further addition causes the acidity to decrease very slowly until the neutral point is reached, when a sudden change takes place. It can be shown that the middle of this steep portion of the curve corresponds to the normal salt, where both acid and base are present in exactly equivalent amounts. For sodium hydroxide and hydrochloric acid this end point comes at the neutral point where  $pH = 7$ . When weak acids or bases are used the end point corresponding to equivalent amounts of acid and base will not come at a  $pH$  of 7 because the salts produced by the neutralization are hydrolyzed as explained later on page 488.

Similar curves showing the variation in hydrogen-ion activity on

titrating some typical alkaline solutions with hydrochloric acid are plotted in Fig. 124.

It will be noted that there are two end points in the sodium carbonate curve, the first corresponding to the formation of bicarbonate ion,

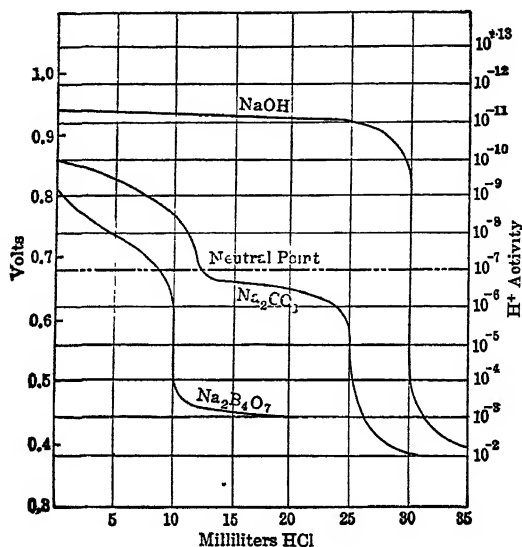
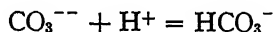
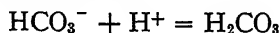


FIG. 124

and the second to that of carbonic acid. The first is represented by the equilibrium



and the second by the equilibrium



It was known empirically, long before these titration curves were obtained, that phenolphthalein is a suitable indicator for the carbonate and methyl orange for the bicarbonate. The former changes color at a pH of about 9 and the latter at about 4, corresponding to the steep parts of the curve, and the reason for this choice of indicators is now evident.

The fundamental difference between hydrogen-ion activity as registered by a hydrogen electrode, and the number of milliliters of alkali which are needed to neutralize the acid, must be clearly understood. The latter corresponds to a "reserve" acidity, i.e., to ionized and

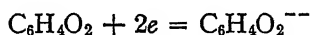
un-ionized acid, but the former gives the actual conditions of acidity, i.e., hydrogen-ion activity. It is of fundamental importance in biology and in many chemical processes.

**Electrodes for Measuring Hydrogen Ions.** The hydrogen electrode described on page 448 is the standard instrument for measuring hydrogen-ion activities, but it is not always suitable. Obviously it cannot be used in solutions of metals which react with platinum and hydrogen. Colorimetric indicators, also, are not always suitable. On account of the practical importance of measuring hydrogen-ion activities under many different conditions, various other electrodes have been devised, and three typical ones will be discussed briefly. Theoretically, any reaction involving hydrogen ions or hydroxyl ions can be used provided a suitable reversible electrode is available.

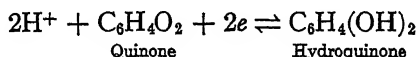
*The Quinhydrone Electrode.* When a little quinhydrone is dissolved in a solution and a platinum or other inert electrode is introduced, the potential of this electrode may be used to determine the activity of hydrogen ions in the solution. A molecule of quinhydrone contains one molecule of quinone and one of hydroquinone. Hydroquinone is a weak acid dissociating slightly according to the reaction



Quinone ( $\text{C}_6\text{H}_4\text{O}_2$ ) may be reduced to hydroquinone ion by the addition of two electrons according to the reaction



Then the hydroquinone ion combines with hydrogen ion to give hydroquinone as shown in the reverse of the first reaction. The whole reaction is



Substituting into equation (8), the quantitative relation is

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{\text{hydroquinone}}}{a_{\text{H}^+}^2 \times a_{\text{quinone}}} \quad [22]$$

Since the concentrations of quinone and hydroquinone are equal because the quinhydrone added contains an equal number of moles of each, the ratio of their activities is nearly unity, and equation (22) becomes

$$E = E_1^0 + 0.0591 \log a_{\text{H}^+} = E_1^0 - 0.0591 pH \quad [23]$$

where  $E_1^0$  is the voltage of the quinhydrone electrode against a hy-

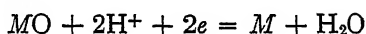
drogen electrode in a solution of unit activity of hydrogen ions. When  $a_{H^+} = 1$  experiment shows that  $E$  is 0.6994. This then is the value of  $E_1^0$ .

When  $E$  is referred to the normal calomel electrode

$$pH = \frac{0.6994 - 0.2801 - E}{0.0591} = \frac{0.4193 - E}{0.0591} \quad [24]$$

The quinhydrone electrode is very simple and convenient and it is not easily poisoned. It is used extensively in industrial operations which demand close control of the  $pH$ . It cannot be used in alkaline solutions (above a  $pH$  of 8.5) on account of the chemical reaction and oxidation of the hydroquinone, and it may not give very accurate results in strong salt solutions because the activity coefficients of the hydroquinone and the quinone may not be exactly the same in such solutions.

*Oxide Electrodes.* Certain metallic oxides of low solubility may be used as hydrogen-ion indicators. For example, with a divalent metal the electrode reaction is



and

$$E_1 = E_1^0 + 0.0591 \log a_{H^+} \quad [25]$$

The constant  $E_1^0$  is evaluated experimentally from solutions of known hydrogen-ion activity using the hydrogen electrode or other reference electrode. The antimony oxide electrode against the hydrogen electrode is used with the formula

$$E_1 = E_1^0 + 0.0591 \log a_{H^+} = 0.144 - 0.0591 pH$$

between  $pH$  5 and 10 when air is excluded and precautions are taken to have the stable, cubic form of the oxide.\*

*The Glass Electrode.* A very thin membrane of glass separating two solutions gives potentials which depend directly on the hydrogen-ion concentrations. The resistance of the glass diaphragm is so great that an electron-tube voltmeter is used to measure the voltages. The membrane is mounted in a cell of the following type:

Calomel electrode || Solution of known  $pH$ ; Glass membrane; Solution of unknown  $pH$  || Calomel electrode

The voltage is a logarithmic function of the difference in hydrogen-ion activity except for a small "asymmetry potential" due to the glass. This may be evaluated by using solutions of known  $pH$  on

\* Roberts and Fenwick, *J. Am. Chem. Soc.*, **50**, 2125 (1928).

each side of the membrane. The glass electrode is not affected by oxidizing solutions, and it can be used in nonaqueous solutions and frequently where the hydrogen electrode cannot be used. This electrode is not suitable for use in strongly alkaline solutions. Improvements in the composition of glass suitable for electrodes together with greater sensitivity to small currents have made possible the use of less fragile glass membranes, and the electron tubes and circuits have been perfected to such a point that the glass electrode is tending to displace other electrodes for the determination of  $pH$  in industrial operations. It finds wide application in control, in biological investigations, and in analytical chemistry.

The mechanism by which the thin glass membrane responds to the hydrogen-ion activity is not thoroughly understood, but it probably involves an adsorption of hydrogen ions on both sides of the membrane, which is in each case proportional to the activity — of the hydrogen ions in the solutions. The theory and use of the glass electrode have been fully treated by Dole.\*

**Other Electrodes.** Electrodes suitable for determining the activity of hydrogen ions have reached a high state of perfection; activities of copper, silver, zinc, and other ions can also be determined with a high degree of precision using metallic electrodes. There is a great need for electrodes which will give the activity of such ions as calcium, sodium, and potassium in complex solutions such as blood. Amalgam electrodes of those metals are suitable in some organic solvents, but they react with water. Dropping electrodes of dilute amalgams have been used with fair success in aqueous solutions. A fresh surface of amalgam is exposed continuously so that changes in composition due to chemical reaction do not have time to affect the potential. These electrodes have not been satisfactory in biological solutions containing proteins.

**Potentiometric Titrations.** In preceding sections it has been shown that activities of ions may be calculated from the potentials of suitable electrodes. Often it is necessary to know only the end point in the titrations and the problem then becomes much simpler. It is not necessary to use reversible electrodes, and no theoretical calculations are involved. A reagent is added gradually until the voltage changes rapidly with the addition of a slight amount of reagent. Sometimes the voltage change is so great as to be noted directly on a galvanometer, but more often the voltages  $E$ , as read on a potentiometer, are plotted against the volume  $V$  of reagent added and the steepest part of the curve is located by inspection. Examples were given in Fig. 123.

\* Dole, "The Glass Electrode," John Wiley and Sons, New York, 1941.



Two or more points of inflection of this type may occur, due to polybasic acids, as shown in Fig. 124, or to mixtures. Sometimes the point of inflection in the curve is not sufficiently pronounced to determine accurately, and then it is helpful to plot tangents of the curve,  $\Delta E/\Delta V$ , against the volume  $V$  of reagent added as shown in Fig. 125. The sharp peak in this curve gives the end point with certainty. The differential graph may be obtained by drawing tangents at points on

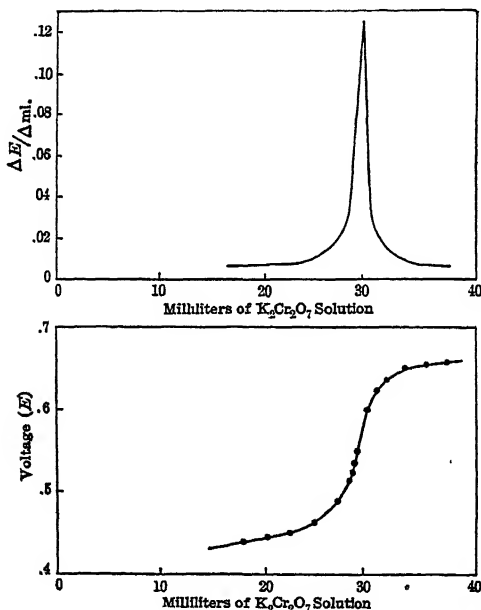


FIG. 125

the voltage curve, or it may be obtained directly from the original data by dividing the differences in voltage by the corresponding differences in milliliters.

Potentiometric titrations do not demand the greatest accuracy in voltage measurements, and a simple voltmeter-potentiometer similar to that shown in Fig. 121 is usually satisfactory. An ordinary platinum wire is simply immersed in the solution for oxidation-reduction titrations. It constitutes one electrode, and the calomel reference electrode is the other.

In addition to neutralizations and oxidations it is possible to obtain end points in precipitations. The titration of iodide with silver nitrate is a simple example. A silver wire is placed in the solution and connected to a calomel reference electrode through a galva-

nometer which is set at zero by balancing against it an equal potential from a battery and adjustable rheostat. As the silver solution is added, the galvanometer remains near zero because the silver-ion concentration is fixed by the solubility of silver iodide. When all the iodide is precipitated, however, the next drop increases the silver-ion concentration enormously and the galvanometer is deflected sharply. A different end point is obtained for bromides, and the two may be titrated together in the same solution.

*Differential titration* is capable of good accuracy. A small part of the original solution is isolated around one of two electrodes (platinum wires) and, as the titration proceeds, the greatest difference in potential between the two electrodes for a given addition of titrant is registered at the end point,\* for then the ratio of the two different concentrations is greatest.

**Junction Potentials.** In addition to the potentials at the two electrodes, already discussed, there is a third potential if two different solutions are in contact with each other. If, for example, a concentrated solution of hydrochloric acid touches a dilute solution, both hydrogen ions and chloride ions tend to diffuse from the concentrated solution into the dilute solution. The hydrogen ion moves faster and thus the dilute solution soon becomes positively charged on account of an excess of positive hydrogen ions. The more concentrated solution is left with an excess of negative chloride ions and thus acquires a negative charge. The differential diffusion is soon offset by the charges set up.

In general, it may be stated that the difference of potential set up at the junction of the two solutions is caused by the difference in the rates of migration of the two ions, *the more dilute solution acquiring a charge corresponding to that of the faster-moving ion.*

The difference in potential at the junction of two liquids must be eliminated or corrected in making accurate measurements of electrode potentials. The most convenient way of minimizing this potential is through the use of a salt bridge of potassium chloride connecting the two solutions of different electrolytes.

Potassium chloride is used because the transference numbers of the two ions are about the same, 0.48 for  $K^+$  and 0.52 for  $Cl^-$ . Under these conditions each ion moves with nearly the same velocity and each has the same tendency to give its charge to the more dilute solution.

Other ions than potassium and chloride are usually present at the two ends of the bridge, and it is desirable to minimize the effect of

\* MacInnes and Cowperthwaite, *J. Am. Chem. Soc.*, **51**, 1119 (1929).

these ions by having a large excess of the potassium chloride. For this purpose saturated potassium chloride is more effective than normal potassium chloride in eliminating the junction potential, but it is more troublesome to use. When potassium chloride cannot be used, as, for example, in a cell containing silver nitrate, a salt bridge of ammonium nitrate is used.

The junction potential  $E_j$  may be largely eliminated as just described, or it may be calculated with the help of the following equation

$$E_j = \frac{v_a - v_c}{v_a + v_c} \frac{RT}{nF} \ln \frac{a_2}{a_1} \quad [26]$$

where  $a_2$  is the activity of the ions in the concentrated solution,  $a_1$  is the activity in the dilute solution, and  $v_c$  and  $v_a$  are the migration velocities of the cation and anion, respectively. This formula applies to cells with metal electrodes which are reversible with respect to the cation. Its derivation is not given here.

*Example 12.* Calculate the junction potential when a solution of copper nitrate having  $a_{\text{Cu}^{++}} = 0.1$  is in contact with a solution having  $a_{\text{Cu}^{++}} = 0.001$ .

$$E_j = \frac{v_a - v_c}{v_a + v_c} \frac{RT}{nF} \ln \frac{a_2}{a_1} = \frac{0.00074 - 0.00036}{0.00074 + 0.00036} \times \frac{0.0591}{2} \log \frac{0.1}{0.001} = 0.0204 \text{ volt}$$

When the concentrations of the two solutions are the same but only one ion is common to both solutions, the junction potential can be estimated by the following empirical formula\*

$$E_j = \frac{RT}{nF} \ln \frac{\Lambda_2}{\Lambda_1} \quad [27]$$

where  $\Lambda_2$  and  $\Lambda_1$  are the equivalent conductances of the two electrolytes.

The evaluation of the junction potential constitutes one of the most difficult problems of electrochemistry. It cannot be calculated with the exactness now demanded in electrochemical measurements; yet it must be known in order to calculate the activity of ions. Particularly in the electrochemistry of nonaqueous solutions, ignorance of junction potentials constitutes a serious handicap. These potentials may be quite large. Nevertheless the uncertainty need not prevent their use in an empirical way for practical, useful measurements, particularly if the measurements involve *differences* in concentration, for then the junction potential is largely canceled out.

**Activity of Electrolytes and Ions.** The term *activity* may be defined as that quantity which, when substituted for the concentration of a given substance in the mass-action equation, will express its effect in

\* Lewis and Sargent, *J. Am. Chem. Soc.*, **31**, 363 (1909).

determining the equilibrium. The simple equations which apply only in dilute solutions may be made applicable also to concentrated solutions by substituting activities, or effective concentrations, for analytically determined concentrations. A similar situation was met with on page 293. This simple artifice is not quite as fundamental as it might appear at first sight, for a new and unknown variable, the activity coefficient  $\gamma$ , has been introduced. However, this activity coefficient may be determined experimentally in a number of different ways (in terms of appropriate conventions), and it is a great advantage to be able to use such equations with exactness even if the evaluation of the new quantity is sometimes rather difficult. Methods for determining activities will be given in Chapter XVIII.

The results are shown for solutions of potassium chloride in Table VI where the ratios of analytically determined concentrations are given in the first column and the activities, as determined from electromotive force measurements, are given in the second column. The ratio of concentrations is always 10, but the ratio of activities is less than 10. It approaches 10, however, as the concentration is decreased. In very dilute solutions the activities become identical with the concentration (because activity is arbitrarily defined in this way).

TABLE VI

RATIOS OF ION CONCENTRATIONS IN SOLUTIONS OF POTASSIUM CHLORIDE

$c_2/c_1$ (Concentration Ratio)	$a_2/a_1$ (Electromotive Force)
0.5 : 0.05	8.09
0.1 : 0.01	8.33
0.05 : 0.005	8.64
0.01 : 0.001	9.04

The activity of a uni-univalent electrolyte may be defined as the product of the ionic activities:

$$a_+ \times a_- = a_{\text{solute}} \quad [28]$$

The activity coefficients  $\gamma_+$  and  $\gamma_-$  of the ions are defined as the ratios of the activities of the ions to their molal concentrations.

$$\gamma_+ = \frac{a_+}{m} ; \gamma_- = \frac{a_-}{m} \quad [29]$$

By definition the activity coefficient  $\gamma$  of the electrolyte is

$$\gamma = (\gamma_+ \times \gamma_-)^{1/2} \quad [30]$$

for a uni-univalent electrolyte, and hence for a uni-univalent electrolyte

$$a_{\text{solute}} = m\gamma_+ \times m\gamma_- = m^2\gamma^2 \quad [31]$$

In dilute solutions it may be considered that the ionic activities are approximately

$$a_+ = a_- = m\gamma \quad [32]$$

For other than a uni-univalent electrolyte the expressions are slightly more complicated. Thus for a salt of the  $\text{CaCl}_2$  type,

$$a_{\text{CaCl}_2} = a_{\text{Ca}^{++}} \times a_{\text{Cl}^-}^2 \quad [33]$$

If the molality of  $\text{CaCl}_2$  is  $m$ , the  $\text{Ca}^{++}$  concentration is  $m$  and the  $\text{Cl}^-$  concentration  $2m$ . Therefore

$$\gamma_+ = \frac{a_+}{m}; \quad \gamma_- = \frac{a_-}{2m} \quad [34]$$

Also

$$\gamma = (\gamma_+ \times \gamma_-^2)^{1/3} \quad [35]$$

Finally,

$$a_{\text{CaCl}_2} = (m\gamma_+)(2m\gamma_-)^2 = 4m^3\gamma^3 \quad [36]$$

The extension to other types of electrolytes is similar.

A formula for concentration cells of *uni-univalent* electrolytes involving both ions, similar to equation (11) for a single ion, may be written in the form

$$E = -\frac{RT}{nF} \ln \frac{a_+'}{a_+''} - \frac{RT}{nF} \ln \frac{a_-'}{a_-''} = -\frac{RT}{nF} \ln \frac{a_+' \times a_-'}{a_+'' \times a_-''} \quad [37]$$

where the single and double primes denote the activities of the solute at two different concentrations. This equation applies only to cells in which the electrodes are reversible with respect to both cation and anion.

Since  $a_+ \times a_- = (m\gamma)^2$ , it follows that equation (37) may be written in the form

$$E = -\frac{2RT}{nF} \ln \frac{m'\gamma'}{m''\gamma''}$$

which, at  $25^\circ$ , becomes, on passing to Briggsian logarithms

$$E = -0.1182 \log \frac{m'\gamma'}{m''\gamma''} \quad [38]$$

The activity coefficient at infinite dilution is defined as unity. If  $m'$  is exceedingly small  $\gamma'$  is 1, and  $\gamma''$  may be obtained from equation (38)

when  $E$ ,  $m'$ , and  $m''$  are known. More details are given on page 526. In this general manner the activity coefficients of the electrolytes given in Table VII have been determined.

TABLE VII  
ACTIVITY COEFFICIENTS AT 25°

Molality	HCl	KCl	NaCl	NaOH	H <sub>2</sub> SO <sub>4</sub>	CaCl <sub>2</sub>	CdSO <sub>4</sub>
0.005	0.930	0.927	0.928	....	0.643	0.789	.....
0.01	0.906	0.902	0.903	0.89	0.545	0.732	0.476
0.05	0.833	0.817	0.821	0.80	0.341	0.584	0.383
0.10	0.798	0.770	0.778	0.75	0.266	0.524	0.199
0.20	0.768	0.719	0.732	0.71	0.210	0.491	0.137
0.50	0.769	0.652	0.680	0.68	0.155	0.510	0.061
1.00	0.811	0.607	0.656	0.66	0.131	0.725	0.042
2.00	1.011	0.578	0.670	0.68	0.125	1.554	0.030
3.00	1.31	0.574	0.719	....	0.142	3.384	0.026
4.00	1.74	.....	0.791	....	0.172	.....	.....

It will be noted that the activity coefficients of these electrolytes pass through a distinct minimum value but that the minima do not occur at the same concentration for each solute. In Fig. 126 the activity coefficients of these typical electrolytes are plotted against the square root of the ionic strength, a term which will be defined later on page 500.

Usually the activity coefficients are less than 1, and the effective concentration is less than the analytically determined value. Sometimes, as in concentrated solutions of hydrochloric acid or calcium chloride, or in nonaqueous solutions, the activity coefficients are found to be much greater than 1. It is of doubtful value to offer a mechanism for activities, but this effective concentration, so much greater than the stoichiometric concentration, may be attributed to a change in the solvent. The effective concentration may be increased by removing solvent quite as well as by increasing the amount of dissolved solute. As shown in Fig. 126, calcium chloride, which crystallizes out with water of crystallization, may very likely render some of the water inactive as a solvent and thereby make the effective concentration greater in concentrated solutions than the analytically determined concentration. In very concentrated hydrochloric acid solution the high value of the activity coefficient  $\gamma$  probably is due to the presence of hydrochloric acid molecules which are absent in dilute solutions.

The activity coefficients of a large number of electrolytes, both alone

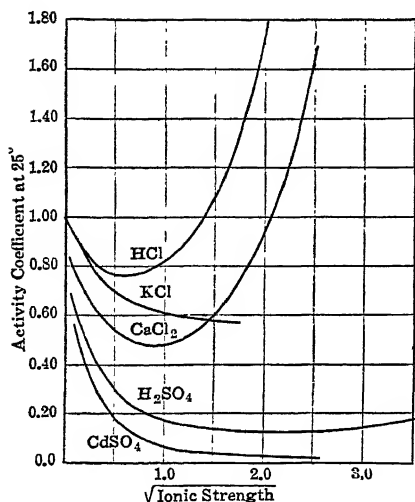


FIG. 126

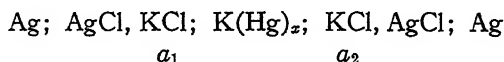
and mixed, in solutions of varying concentrations have been determined with a high degree of accuracy.\*

**Cells with and without Transference.** Cells which contain a liquid junction potential are called cells *with transference*. Those which do not contain a liquid junction are called cells *without transference*. Through the use of a potassium chloride salt bridge it is possible to reduce greatly the junction potential. Although cells with salt bridges have great practical value, as for example in the case of the hydrogen electrode, they are

not and probably never will be thermodynamically exact.†

The cells without liquid junctions are free from this difficulty of the junction potential and are thermodynamically exact, but they are often difficult to devise. Moreover, since they are reversible with respect to both ions the potential of the cell gives the mean activity of both positive and negative ions, and absolute information concerning either one alone is not available. They are used for measuring accurately the mean activities of electrolytes.

Concentration cells may be used either without or with transference. Two cells may be combined into a cell without transference by using an amalgam in a compartment which is connected with two different solutions as follows



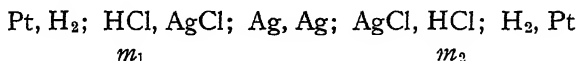
This cell is in reality made up of two independent cells and involves no liquid junction. The molalities of the potassium chloride in the two solutions are  $m_1$  and  $m_2$ , and the activity coefficients are  $\gamma_1$  and  $\gamma_2$ . The electromotive force is given by equations (37) and (38) thus

$$E = -2 \frac{RT}{nF} \ln \frac{m_2 \gamma_2}{m_1 \gamma_1} \quad [39]$$

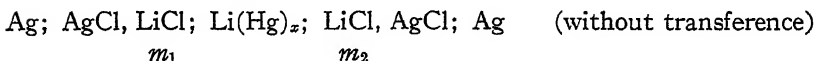
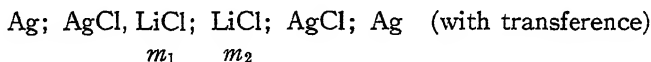
\* Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931, pp. 763-825; MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939, p. 167.

† Guggenheim, *J. Phys. Chem.*, **34**, 1758 (1930).

Cells without liquid junctions may also be arranged with a metallic conductor between the two cells, as in the following case, using silver chloride electrolytes:



If two concentration cells are arranged one with transference and one without transference there will be a difference in electromotive force on account of the junction potential. This in turn is determined by the transference number. For example, in the following cells, the electrodes of silver chloride are reversible with respect to the chloride ion



It can be shown\* that in a cell with transference, which is reversible to the anion

$$E_t = - \frac{2n_c \dagger RT}{nF} \ln \frac{m_2 \gamma_2}{m_1 \gamma_1} \quad [40]$$

Dividing equation (40) by (39)

$$n_c = \frac{E_t}{E} \quad [41]$$

Using this formula for data obtained in the lithium cell just described the transference number of lithium ion in 0.01 molal solution was found to be 0.334† in close agreement with the value 0.332 found by other methods.

**The Lead Storage Cell.** Storage cells are devices for the storage of electrical energy in the form of chemical energy. Any reversible cell may be employed as a storage cell, but the lead storage cell is the one now in general use.

If two lead plates are immersed in a 20 per cent solution of sulfuric acid, a trace of lead sulfate is formed on the surface of each plate. If a current of electricity is passed through the solution, the lead sulfate

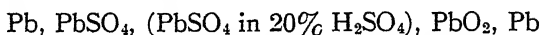
\* The potentials of the two electrodes and the junction potential are added together for the emf. of the whole cell. MacInnes "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939, pp. 222-225.

† The term  $2n_c$  does not appear in the formulas given before for cells with transference because the junction potential was practically eliminated with a potassium chloride bridge.

‡ MacInnes and Beattie, *J. Am. Chem. Soc.*, **42**, 1117 (1920).

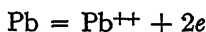


on the cathode undergoes reduction to metallic lead, and the lead sulfate on the anode is oxidized to lead peroxide. In this manner, the following cell is formed:

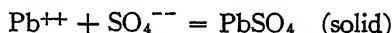


The electromotive force of this cell is about 2 volts. The amounts of lead and lead peroxide produced in this way are so small that when used as a source of electricity the cell has a very small capacity. In order to increase its capacity, the electrodes are given as large a surface as possible. This increased surface is produced by electrolyzing, first in one direction and then in the other, thus causing the plates to become spongy; or by filling a lead "grid" with a paste of lead oxide and red lead, and electrolyzing until spongy lead is formed at the cathode and lead peroxide is formed at the anode. If the charging circuit is broken and the two electrodes are connected by a wire, electrons will flow through the wire from the lead plate to the peroxide plate, and lead sulfate tends to form on each electrode.

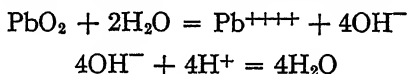
The operation of the cell may be described in more detail. At the *negative electrode* the lead ionizes to give plumbous ions, leaving behind free electrons which then pass through the wire to the positive electrode, thus



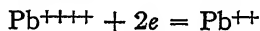
This reaction is followed by the reaction



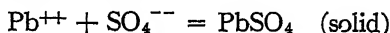
At the *positive electrode* the lead peroxide dissolves slightly and dissociates in the sulfuric acid solution to give plumbic ions and water



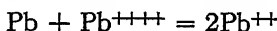
The important electrochemical reaction at the positive electrode is



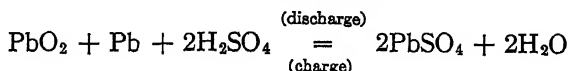
It is followed by the reaction



The fundamental ionic reaction of the lead storage cell is simply



The total chemical reaction may be summarized as follows:



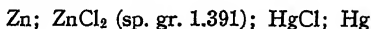
On open circuit there is no reaction because the high overvoltage of hydrogen on lead prevents chemical action with the acid. Impurities in the lead electrodes or impurities precipitated from the electrolyte solution set up local action so that the cell does not remain charged indefinitely. Also there is some electrical leakage across the cover of the cell. Cells should never be permitted to remain discharged, but as soon as the voltage drops to 1.80 volts they should be recharged immediately. When allowed to stand in a discharged condition for any length of time, "sulfating" occurs, i.e., hard crystals of lead sulfate are formed on the plates, thereby rendering subsequent attempts to recharge the cell exceedingly difficult. Cells should be charged until the voltage becomes constant and gas is freely evolved. The specific gravity of the electrolyte of a fully charged storage cell is 1.210 to 1.215.

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- MACINNES, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939.  
 GLASTONE, "Introduction to Electrochemistry," D. Van Nostrand Co., New York, 1942.  
 DOLE, "Experimental and Theoretical Electrochemistry," McGraw-Hill Book Co., New York, 1935.  
 LATIMER, "Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, New York, 1938.  
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## PROBLEMS

## 1. The electromotive force of the cell



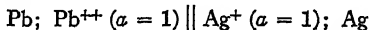
is 1.0000 volt at 15° and 1.00047 volts at 20°. What is the average heat of the reaction



between 15° and 20°

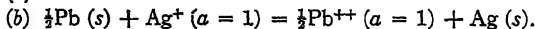
$$\text{Ans. } \Delta H = -44,865 \text{ cal.}$$

## 2. Given the cell at 25°



(a) calculate the potential; (b) write the cell reaction; and (c) calculate the free energy change.

$$\text{Ans. } (a) 0.925.$$



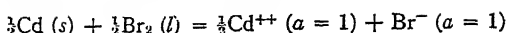
$$(c) -21,330 \text{ cal.}$$

3. (a) Calculate the potential of the following cell, and (b) state which is the negative electrode.



$$\text{Ans. } (a) 0.2936. (b) \text{Pt}; \text{Br}_2 (l); \text{Br}^-.$$

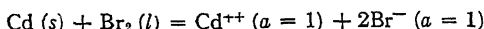
4. (a) Construct a cell in which the reaction is:



(b) What is the potential of the cell?

(c) What is the free energy of the reaction?

(d) What difference would there be in the solution of this problem if the reaction were written



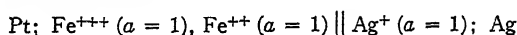
Ans. (a)  $\text{Cd}; \text{Cd}^{++}(a=1) \parallel \text{Br}^-(a=1), \text{Br}_2(l)$

(b) 1.4672 volt.

(c) -33,818.

(d) (a) and (b) would be the same; (c) would be -67,636.

5. Write the reaction of the cell

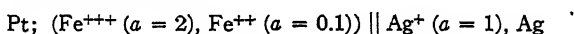


Calculate (a) the cell potential and (b) the free energy of the reaction at 25°. (c) What is the value of the equilibrium constant? (d) What would be the activity of  $\text{Ag}^+$  ions in equilibrium with solid silver in a solution containing  $\text{Fe}^{+++}$  and  $\text{Fe}^{++}$  at unit activity?

Ans. (a)  $E^\circ = 0.016$ . (b)  $\Delta F^\circ = -369$  cal.

(c)  $K = 1.86$ . (d)  $a_{\text{Ag}^+} = 0.54$ .

6. Write the reaction of the cell



Calculate (a) the cell voltage and (b) the free energy change  $\Delta F$  at 25°.

Ans. (a) -0.0609. (b) 1405.

7. The free energy of formation  $\Delta F^\circ_{298.15K}$  of  $\text{Pb}^{++}$  is -5,630 cal. The free energies of formation of the elements and of hydrogen ion at unit activity are taken as zero. Calculate the potential of the cell at 25°.



Ans. 0.122.

8. The concentration of  $\text{AgNO}_3$  in a solution was changed from 0.001 to 0.0001 moles per 1000 g. of water. How much will the electrode potential of a silver electrode immersed in the solution change at 25°, assuming the activity coefficient in a dilute solution to be 1?

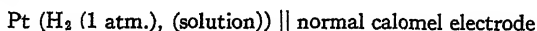
Ans. 0.059 volt.

9. (a) What is the activity of hydrogen ions in a solution which has a pH of 7.7 at 25°?

(b) Calculate the pH of a solution which has a hydrogen-ion activity of 2.0 equivalents per 1000 g. of water at 25°.

Ans. (a)  $2 \times 10^{-8}$  (b) -0.3.

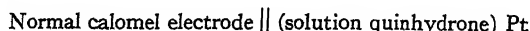
10. An electromotive force of 0.829 volt was obtained at 25° for a solution when placed in the cell



What is the pH of the solution?

Ans. 9.29.

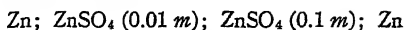
11. The cell



was found to have a potential of 0.179 volt for a certain solution at 25°. What is the pH of the solution?

Ans. 4.07.

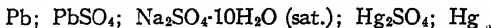
12. What is the voltage of the cell



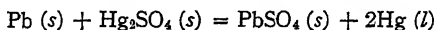
at 25°? For  $\text{ZnSO}_4$ ,  $n_a = 0.6$ , and the activity coefficients of the  $\text{Zn}^{++}$  ion are 0.23 in 0.1  $m$   $\text{ZnSO}_4$  and 0.5 in 0.01  $m$   $\text{ZnSO}_4$ . Ans. 0.024

13. A small flashlight battery weighing 90 g. gives 2.73 ampere-hours at an average voltage of 1.3 volts. *Theoretically* how high could this energy lift the battery above the earth?

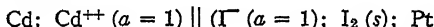
14. The electromotive force of the cell



is 0.9647 volt at 25°. The temperature coefficient is 0.000174 volt per degree. Calculate (a) the heat of the reaction and (b) the free energy change of the reaction,

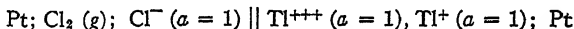


15. Given the cell at 25°



(a) calculate  $E^0$ ; (b) write the cell reaction; (c) calculate  $\Delta F^0$ .

16. Given the cell at 25°



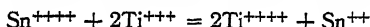
(a) Write the cell reaction.

(b) Calculate  $\Delta F^0$ .

(c) Calculate the equilibrium constant for the cell reaction.

(d) Calculate  $E$  for the cell when the chloride ion activity is 0.1 instead of 1.

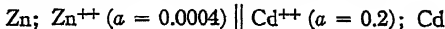
17. (a) Calculate the equilibrium constant for the reaction



(b) When 0.01 mole of stannous ion is added to 1.0 mole of  $\text{Ti}^{++++}$  ion in 1000 g. of water, what will be the concentration of  $\text{Ti}^{+++}$  ions (assuming for the calculation that the activities are essentially equal to the concentrations)?

18. The standard reduction potential for the reaction  $\text{Fe}^{+++} + e \rightarrow \text{Fe}^{++}$  is 0.783; and for the reaction  $\text{Fe} \rightarrow \text{Fe}^{++} + 2e$  it is 0.441. What would be the standard electrode potential for the reaction  $\text{Fe} = \text{Fe}^{+++} + 3e$ ?

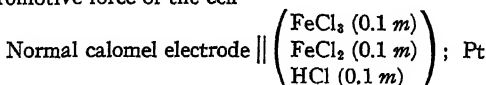
19. (a) Calculate the voltage of the following cell at 25°:



(b) Write the cell reaction.

(c) Calculate the value of the free energy change involved in the reaction of the solutions as given, i.e.,  $\text{Zn}^{++}$  at an activity of 0.0004 and  $\text{Cd}^{++}$  at an activity of 0.2.

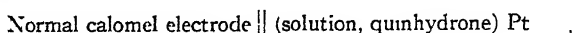
20. The electromotive force of the cell



is 0.446 volt at 25°. The hydrochloric acid is added to prevent hydrolysis. Assuming that the activity coefficients of the  $\text{Fe}^{+++}$  and  $\text{Fe}^{++}$  ions are 0.75 and 0.87, respectively, calculate the value of  $E^0$  for the ferric-ferrous electrode containing 0.1  $m$   $\text{HCl}$ .

21. A hydrogen electrode and a normal calomel cell give an electromotive force of 0.520 when placed in a certain solution at 25°. What is the pH of the solution?

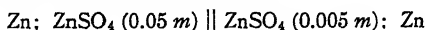
22. The cell



was found to have a potential of 0.263 for a certain solution at 25°. What is the pH of the solution?

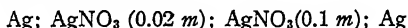
23. To what pH are the following hydrogen-ion activities equal: (a) 0.3, (b)  $10^{-11}$ ? To what hydrogen-ion activities are the following pH values equivalent: (c) 10.6, (d) -1.1?

24. At 25° the electromotive force of the cell



is -0.0217 volt. Assuming the activity coefficient of the Zn ion to be 0.59 in the dilute solution, what is the activity coefficient in the more concentrated solution?

25. What is the potential of the cell



at 25°? For  $\text{AgNO}_3$ ,  $\alpha_a = 0.53$ , and the activity coefficients of silver nitrate are 0.86 in 0.02  $m$   $\text{AgNO}_3$  and 0.72 in 0.1  $m$   $\text{AgNO}_3$ .

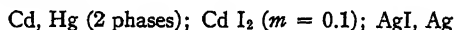
26. The potential at 25° of the cell



is -0.1774. Assuming that the activities and the small junction potentials with the salt bridge remain constant what will be the electromotive force of the cell at 50°?

27. What must be the concentration of  $\text{Cu}^{++}$  ions in order that the deposition potential of copper from solution at 25° will be the same as the deposition potential of zinc from a solution containing  $\text{Zn}^{++}$  ions at unit activity?

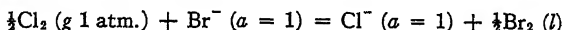
28. For the cell at 25°



Bates [*J. Am. Chem. Soc.*, **63**, 399 (1941)] found  $E = 0.35776$ . When cadmium iodide is at unit activity  $E^0 = 0.20060$ . Calculate the activity coefficient of the cadmium iodide in 0.100 molal solution.

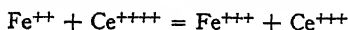
29. Calculate  $\Delta F^0$  and  $\Delta H$  (at 20°) for the reaction which takes place in the standard Weston cell.

30. (a) Construct a cell in which the reaction is



(b) Determine the voltage at 25° and (c) calculate the free energy of the reaction.

31. (a) Construct the cell corresponding to the reaction

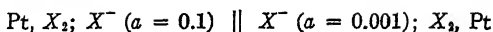


(b) Calculate the standard voltage of the cell at 25°.

(c) Calculate the equilibrium constant.

32. (a) How should a cell be constructed in order to determine  $E^0$  for the cell corresponding to the reaction of  $\text{Cl}_2$  with  $\text{Fe}^{++}$ ? (b) What is the equilibrium constant for the reaction?

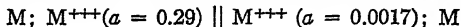
33. Given the cell at 25°



where  $X$  is an unknown halogen:

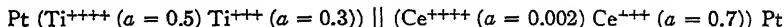
- Write the cell reaction.
- Which electrode is negative?
- What is the voltage of the cell?
- Is the reaction spontaneous?

34. What is the electromotive force of the following cell at 50°

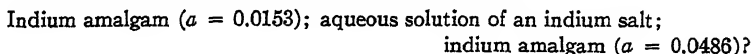


35. Calculate the concentration of mercurous ion in a solution at 25° which was originally 0.001 molal in mercuric ion after enough ferrous iron has been added to give the solution an activity of ferrous ion equal to 0.0002.

36. Calculate the potential of the following cell at 25°



37. (a) What is the electromotive force at 25° of the cell



(b) If the aqueous solution of an indium salt is replaced by an alcoholic solution, will there be a difference in the voltage of the cell?

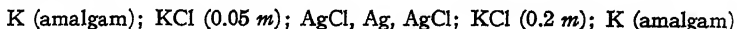
38. What is the activity of zinc ions in a solution which gives with a zinc electrode a potential of  $-0.7500$  volt against the standard hydrogen electrode? What is the molality of the solution if the activity coefficient for the zinc ion is 0.30 at this concentration?

39. A hydrogen electrode and a calomel electrode are placed in a solution having a  $pH$  of 1.2. What is the voltage of the cell?

40. Calculate the  $pH$  of 0.01  $N$  sodium hydroxide solution at 25°. The activity coefficient is 0.75.

41. A hydrogen electrode and calomel cell are used to determine the  $pH$  of a solution on a mountain where the barometer is 500 mm. The hydrogen is allowed to bubble out of the electrode at the atmospheric pressure prevailing there. If the  $pH$  is calculated to be 4.00, what is the correct  $pH$  of the solution?

42. The cell

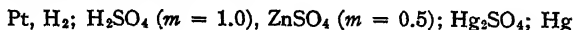


is reversible to both cation and anion. Calculate its potential at 25°, knowing the activity coefficients of potassium chloride.

43. Calculate the activity of  $\text{H}_2\text{SO}_4$  in 0.01 molal solution if the activity coefficient  $\gamma$  is 0.545.

44. An aqueous solution contains silver ions, cadmium ions, and sodium ions. Describe the cathode reactions which will take place as the potential is gradually increased, starting from zero.

45. Tartar, Newschwander, and Ness [*J. Am. Chem. Soc.*, **63**, 28 (1941)] found that the electromotive force of the cell



is 0.67281 volt at 25°.  $E^0 = 0.61515$  volt. Calculate the activity coefficient of sulfuric acid in a solution which is 1 molal with respect to  $H_2SO_4$  and 0.5 molal with respect to  $ZnSO_4$ .

46. Five hundred milliliters of 0.01 molar stannous ion is added to 500 ml. of 0.01 molal ferric ion at 25°. What will be the concentration of each of the four resulting ions? The activities may be considered equal to the concentrations for this calculation.

47. A solution at 25° contains  $Ni^{++}$  ions at an activity of 0.1. If the solution is too acid, hydrogen will be deposited on the cathode instead of nickel. What should be the  $pH$  of the solution so that the hydrogen will not be liberated until the potential is 0.1 volt greater than the potential required to deposit the nickel? The overvoltage of hydrogen on nickel may be assumed to be 0.2 volt.

48. (a) Develop a formula for calculating the potential of a cell consisting of two chlorine electrodes at different pressures immersed in a solution of a chloride.

(b) Calculate the potential if the chlorine of one electrode is at 1 atm. and the other is at 0.25 atm. and the temperature is 25°.

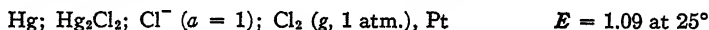
49. At 25° for the reaction



the equilibrium constant is 0.018, and at 35° it is 0.054. What is the value of  $E^0$  at 30° for the cell which corresponds to this reaction?

50. How many grams of solid anhydrous stannous chloride must be added to a liter of 0.01 molar ferric chloride to reduce 99 per cent of the ferric ion? The activities may be considered equal to the concentrations.

51. Formulate the cell reaction for the following cell



Calculate the dissociation pressure of calomel ( $p_{Cl_2}$ ) in atmospheres at 25°.

52. The common Leclanché dry cell consists of an electrode of graphite surrounded by graphite and manganese dioxide immersed in a saturated solution of ammonium chloride (together with zinc chloride and starch) and sealed into a zinc container which acts as the other electrode. Zinc is consumed and hydrogen and ammonia are produced at the graphite electrode.

(a) What happens to the hydrogen and the ammonia?

(b) Write equations for the primary and various secondary reactions.

(c) Explain why the zinc is consumed only when the circuit is closed (except for a slight local action).

## CHAPTER XVII

### IONIC EQUILIBRIA

When electrolytes are dissolved in water they break up into smaller units, as proved by the abnormally large lowering of the freezing point described on page 224. The fact that these solutes, which give abnormally large effects, produce solutions which conduct the electric current proves that the smaller units are electrically charged ions. This relation was discussed on page 225. Further consideration of the quantitative behavior and the significance of these ionic solutions has been deferred until now in order to present first the concepts of chemical equilibrium, the facts of the electrical conductance of solutions, and the study of electrolytes through measurements of electromotive force. The study of ionic equilibria constitutes one of the oldest and most important branches of physical chemistry.

**Ionization of Weak Electrolytes.** The extent to which a weak electrolyte is dissociated may be determined in different ways, among which the electrical conductance method is the most used on account of its accuracy and simplicity. In general, the dissociation becomes greater as the solution is diluted. The recombination of the ions decreases because the number of collisions becomes less. If the solute is not dissociated at all the solution will have a conductance no greater than that of the solvent alone. If it is completely dissociated the equivalent conductance cannot be increased any more by further dilution. The degree of dissociation,  $\alpha$ , at a given concentration is measured by the ratio of the equivalent conductance at that concentration to the equivalent conductance at infinite dilution. Thus

$$\alpha = \frac{\Lambda}{\Lambda_0} \quad [1]$$

This relation was first derived by Arrhenius. It has been shown that at infinite dilution the equivalent conductance  $\Lambda_0$  is equal to the sum of the ionic conductances  $l_c$  and  $l_a$ .

$$\Lambda_0 = l_c + l_a \quad [2]$$

Neglecting the change in velocity of the ions with concentration and



assuming that the only influence of dilution on the equivalent conductance is the production of more ions, Arrhenius stated that at any dilution the equivalent conductance is equal to the sum of the ion conductances multiplied by the degree of dissociation.

$$\Lambda = \alpha l_c + \alpha l_a = \alpha(l_c + l_a) \quad [3]$$

Equation (1) is then obtained by dividing equation (3) by equation (2).

Although satisfactory for weak electrolytes, equation (1) cannot be applied to strong electrolytes in which dissociation is practically complete. The change of equivalent conductance of strong electrolytes with concentration is due to a change in velocity of the ions as described later in this chapter.

Acetic acid is a good example of a weak electrolyte. When dissolved in water it dissociates according to the reaction



If  $c$  moles of acetic acid is dissolved in a liter of water and the degree of dissociation of the acid is  $\alpha$ , then the concentration of hydrogen ions is  $c\alpha$ , the concentration of acetate ions is  $c\alpha$  and the concentration of un-ionized acetic acid molecules is  $c(1 - \alpha)$ . The equilibrium or ionization constant  $K$  is given by the expression

$$K = \frac{c_{\text{H}^+} \times c_{\text{CH}_3\text{COO}^-}}{c_{\text{CH}_3\text{COOH}}} = \frac{c\alpha \times c\alpha}{c(1 - \alpha)} = \frac{\alpha^2 c}{1 - \alpha} \quad [4]$$

If more than two ions are formed the ionization constant will have a different form which may be easily derived.

*Example 1.* The equivalent conductance of a 0.001028 *N* acetic acid solution is found to be 48.15 at 25°. Calculate the degree of dissociation of acetic acid at this concentration and calculate the ionization constant.

$$\alpha = \frac{\Lambda}{\Lambda_0} = \frac{48.15}{390.7} = 0.1232$$

$$K = \frac{\alpha^2 c}{1 - \alpha} = \frac{(0.1232)^2 \times 0.001028}{0.8768} = 1.780 \times 10^{-5}$$

From calculations like this, Table I is obtained using the data of MacInnes and Shedlovsky.\*

The value of  $K$  calculated in this way is reasonably constant, and it is satisfactory for most practical work. There are, however, unsatisfactory assumptions involved in this calculation which are partly

\* MacInnes and Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429 (1932); MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939, p. 56.

compensating. Making a correction for the fact that the ionic conductances are not quite the same as they are at infinite dilution and estimating the activity coefficients of the ions from the Debye-Hückel theory to be discussed later in this chapter on page 504, MacInnes†

TABLE I  
IONIZATION CONSTANT OF ACETIC ACID AT 25°  
( $\Lambda_0 = 390.7$ )

Concentration Equivalents/Liter	Equivalent Conductance	Degree of Dissociation	$K$ Dissociation Constant $\times 10^5$
0 00002801	210.4	0.5385	1.760
0.0001532	112.0	0.2867	1.767
0.001028	48.15	0.1232	1.781
0.002414	32.22	0.08247	1.789
0 005912	20.96	0.05365	1.798
0 01283	14.37	0.03678	1.803
0 05000	7.36	0.01884	1.808

shows that these dissociation constants have values ranging from 1.752 at 0.0002801  $N$  to 1.721 at 0.05000  $N$ . In this revised calculation  $\Lambda_0$  for acetic acid is not used but a value of the equivalent conductance for complete dissociation is obtained at the given concentration by a method similar to that illustrated by example 5 on page 408 in which  $\Lambda_{NaCl}$  is subtracted from the sum of  $\Lambda_{HCl}$  and  $\Lambda_{NaC_2H_3O_2}$ , it being assumed that these electrolytes are completely dissociated.

With the help of equation (4) it is possible to calculate at any concentration  $c$  the degree of dissociation of acetic acid or any other weak electrolyte which dissociates into two ions. When the electrolyte is weak, i.e.,  $K$  is  $10^{-4}$  or  $10^{-5}$  or less, the term  $(1 - \alpha)$  does not differ appreciably from unity and equation (1) becomes

$$K = \alpha^2 c$$

and

$$\alpha = \sqrt{\frac{K}{c}} \quad [5]$$

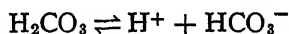
*Example 2.* Calculate the concentration of hydrogen ions in a solution which contains 0.0700 mole of acetic acid in 500 ml. of water solution. It is convenient to convert the data into terms of moles per liter. The original concentration  $c_0$  is then 0.140 mole per liter. Let  $x$  equal the number of moles of acetic acid

† MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939, pp. 342-348.

ionized per liter and assume that for weak acids  $c_0 - x$  is essentially equal to  $c_0$ . Approximately,

$$\begin{aligned} K &= 1.80 \times 10^{-5} \\ &= \frac{c_{\text{H}^+} \times c_{\text{C}_2\text{H}_3\text{O}_2^-}}{c_{\text{HC}_2\text{H}_3\text{O}_2}} = \frac{x^2}{c_0} = \frac{x^2}{0.140} \\ x^2 &= 1.80 \times 10^{-5} \times 0.140 = 2.52 \times 10^{-6} \\ x &= 1.59 \times 10^{-3} \\ \text{More exactly} \quad x^2 &= 1.80 \times 10^{-5}(0.140 - x) \\ &= 1.80 \times 10^{-5}(0.140 - 0.00159) \\ &= 2.492 \times 10^{-6} \\ x &= 1.58 \times 10^{-3} \end{aligned}$$

Although these formulas are derived on the assumption that the electrolytes dissociate into only two ions, as a matter of fact they apply fairly well also to di- and tribasic acids because they dissociate in steps. The first hydrogen ion ionizes much more readily than the second or third hydrogen in a polybasic acid. Thus in the electrolytic dissociation of carbonic acid the first hydrogen ion comes off according to the reaction



in which

$$K = 4.54 \times 10^{-7}$$

but the second hydrogen ion has to pull away from an ion with two negative charges instead of one. Accordingly the degree of dissociation is considerably less and the dissociation constant is smaller, thus



Ionization constants for a number of acids are given in Table II.

The dissociation of bases to give hydroxyl ions has also been the subject of extensive study. The alkali and alkaline earth hydroxides are very strong bases, and are dissociated to about the same extent as equivalent solutions of hydrochloric and nitric acids, while, on the other hand, ammonia and many of the organic bases are very weak. Table III gives the ionization constants of several typical bases.

The ionization of bases and acids may be determined experimentally in several different ways: from measurements of electrical conductance or of electromotive force, from measurements of the concentration of the hydrogen or hydroxyl ions as described in Chapter XVI, and

TABLE II

IONIZATION CONSTANTS OF ACIDS IN WATER AT 25°

Acid	Ionization Constant
Iodic, $\text{HIO}_3$	$2 \times 10^{-1}$
Dichloroacetic, $\text{CHCl}_2\text{COOH}$	$5.2 \times 10^{-2}$
Monochloroacetic, $\text{CH}_2\text{ClCOOH}$	$1.5 \times 10^{-3}$
Formic, $\text{HCOOH}$	$2.1 \times 10^{-4}$
Acetic, $\text{CH}_3\text{COOH}$	$1.8 \times 10^{-5}$
Carbonic $K_1$ , $\text{H}_2\text{CO}_3$	$4.54 \times 10^{-7}$
$K_2$ , $\text{HCO}_3^-$	$5.61 \times 10^{-11}$
Hydrocyanic acid, $\text{HCN}$	$7.2 \times 10^{-10}$
Boric $K_1$ , $\text{H}_3\text{BO}_3$	$5.8 \times 10^{-10}$
$K_2$ , $\text{H}_2\text{BO}_3^-$	$2 \times 10^{-13}$
$K_3$ , $\text{HBO}_3^{--}$	$2 \times 10^{-14}$
Water, $\text{H}_2\text{O}$	$1.8 \times 10^{-16}$
Ethane, $\text{C}_2\text{H}_6$	Approx. $10^{-34}$

from measurements of the rate of reactions catalyzed by these ions. For example, the rate of inversion of cane sugar provides a means of determining the concentration of hydrogen ions, and the rate of condensation of acetone enables one to determine the concentration of hydroxyl ions.

TABLE III

IONIZATION CONSTANTS OF BASES AT 25°

Base	Ionization Constant
Guanidine	$3 \times 10^{-1}$
Piperidine	$1.3 \times 10^{-3}$
Methylamine	$4.0 \times 10^{-4}$
Trimethylamine	$6.2 \times 10^{-5}$
Ammonia	$1.8 \times 10^{-5}$
Pyridine	$1.6 \times 10^{-9}$
Aniline	$4.2 \times 10^{-10}$

In comparing the acidity of different acids, it is the hydrogen-ion concentration which is significant. In weak acids this is proportional to the square root of the dissociation constants as shown by equation (5).

*Example 3.* Compare the acidity of monochloroacetic acid with that of acetic acid at 25°.

$$\frac{\alpha_{\text{CClH}_2\text{COOH}}}{\alpha_{\text{CH}_3\text{COOH}}} = \frac{\sqrt{K_{\text{CClH}_2\text{COOH}}/c}}{\sqrt{K_{\text{CH}_3\text{COOH}}/c}} = \frac{\sqrt{0.00155}}{\sqrt{0.0000180}} = 9.3$$

**Molecular Structure and Ionization.** In example 3 it is seen that replacing one of the hydrogen atoms on the first carbon with the negative chlorine atom makes it 9.3 times as easy for the hydrogen of the carboxyl group to break away and form a hydrogen ion. Apparently the attraction of chlorine for electrons pulls the electron pair farther away from the hydrogen of the carboxyl and permits the hydrogen ion to leave with the expenditure of less energy. The ionization constants of other substituted acids are given in Table IV.

TABLE IV  
SUBSTITUTED ACETIC ACIDS

Acid	Ionization Constant (25°)
Acetic, $\text{CH}_3\text{COOH}$	0.000018
Propionic, $\text{CH}_3\text{CH}_2\text{COOH}$	0.000013
Monochloroacetic, $\text{CH}_2\text{ClCOOH}$	0.00155
Dichloroacetic, $\text{CHCl}_2\text{COOH}$	0.052
Trichloroacetic, $\text{CCl}_3\text{COOH}$	0.2
Monobromoacetic, $\text{CH}_2\text{BrCOOH}$	0.00138
Cyanoacetic, $\text{CH}_2\text{CNCOOH}$	0.00370
Glycolic, $\text{CH}_2\text{OHCOOH}$	0.000152
Phenylacetic, $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$	0.000056

This table affords an interesting illustration of the influence of different substituents on the strength of acetic acid. Thus, the strength of the acid is increased by the replacement of alkyl hydrogen atoms by Cl, Br, CN, OH, or  $\text{C}_6\text{H}_5$ , while the substitution of the  $\text{CH}_3$  group diminishes its strength.

The influence of a substituent group on the strength of an organic acid is conditioned by its distance from the carboxyl group. This is well illustrated by the ionization constants of propionic acid and some of its derivatives. The effect of the OH group in the  $\alpha$  position is seen to be much more marked than in the  $\beta$  position.

TABLE V  
PROPIONIC ACID DERIVATIVES

Acid	Ionization Constant (25°)
Propionic acid, $\text{CH}_3\text{CH}_2\text{COOH}$	0.0000134
$\alpha$ -hydroxypropionic acid, $\text{CH}_3\text{CHOHCOOH}$ (Lactic acid)	0.000138
$\beta$ -hydroxypropionic acid, $\text{CH}_2\text{OHCH}_2\text{COOH}$	0.0000311

The position of a substituent in the benzene nucleus exerts a marked influence on the strength of the derivatives of benzoic acid. The ion-

ization constants of benzoic acid, and the three chlorobenzoic acids, are given in Table VI.

TABLE VI  
BENZOIC ACID DERIVATIVES

Acid	Ionization Constant (25°)
Benzoic acid, $C_6H_5COOH$	0 000073
<i>o</i> -Chlorobenzoic acid, $C_6H_4ClCOOH$	0 00132
<i>m</i> -Chlorobenzoic acid, $C_6H_4ClCOOH$	0 000155
<i>p</i> -Chlorobenzoic acid, $C_6H_4ClCOOH$	0 000093

When the halogen enters the ortho position, the strength of the acid is greatly augmented; in the meta and para positions, the effect is much smaller, meta-chlorobenzoic acid being stronger than para-chlorobenzoic acid. It is a general rule that the influence of substituents is always greatest in the ortho position, and least in the meta and para positions, the order in the two latter being uncertain.

The influence of molecular structure on the ionization constant and other thermodynamical properties is now finding interpretation in the electron theory (page 645).\*

**Repression of Ionization by Salt.** Just as the dissociation of a gaseous substance is diminished by the addition of an excess of one of the products of dissociation, so the ionization of a weak acid is repressed by the addition of a salt formed from the acid and a strong base. The salts are almost completely dissociated and the addition of the extra anions drives the equilibrium back to give more undissociated acid. For example, a solution of a weak acid,  $HA$ , is made much less acid by the addition of the sodium salt of the acid. The quantitative treatment follows for the reactions,



The concentration of the salt is represented by  $c_s$ . Since salts are generally completely ionized  $c_s$  is also the concentration of the ions produced by the ionization of the salt. The total concentration of the weighed-out acid  $HA$ , including both undissociated and dissociated acid, is designated by  $c_0$ , and the degree of dissociation of the acid is designated by  $\alpha_0$ . The concentration of the undissociated acid is represented by  $c_{HA}$ . Then

$$c_{H^+} = \alpha_0 c_0; \quad c_{A^-} = \alpha_0 c_0 + c_s$$

\* The electron theory in organic chemistry is summarized by Johnson in Gilman's "Organic Chemistry," John Wiley and Sons, New York, 1938, Chapter 19.

and

$$c_{HA} = (1 - \alpha_0)c_0$$

$$K = \frac{c_{H^+}c_{A^-}}{c_{HA}} = \frac{\alpha_0 c_0 \times (\alpha_0 c_0 + c_s)}{(1 - \alpha_0)c_0}$$

For weak acids  $\alpha_0$  is so small that  $\alpha_0 c_0$  is negligible in comparison with  $c_s$ ; and  $1 - \alpha_0$  is practically equal to unity. Then

$$K = \alpha_0 c_s$$

or

$$\alpha_0 = \frac{K}{c_s} \quad [6]$$

In other words, the degree of ionization of a weak acid in the presence of a salt containing a common ion is approximately independent of the concentration of the acid, and it is inversely proportional to the concentration of the added salt.

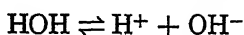
*Example 4.* In example 2 it was calculated that 0.140 mole of acetic acid per liter gave a hydrogen-ion concentration of  $1.6 \times 10^{-5}$  gram-ions per liter. If 0.1 mole of solid sodium acetate is dissolved in a liter of this solution, approximately what will be the concentration of hydrogen ions, assuming that the volume of the solution remains practically unchanged?

$$K = 1.80 \times 10^{-5} = \frac{c_{H^+} \times c_{C_2H_3O_2^-}}{c_{HA}} = \frac{c_{H^+} \times 0.1}{0.140}$$

$$c_{H^+} = \frac{1.80 \times 10^{-5} \times 0.14}{0.100} = 2.52 \times 10^{-5}$$

Similar considerations hold for the addition of a salt to a weak base, thus making the base still weaker. Practical use is made of this repression of ionization. For example, certain metal hydroxides, such as magnesium hydroxide, are precipitated by ammonium hydroxide, but when ammonium chloride is added, the ionization of ammonium hydroxide becomes so slight that there are not then enough hydroxyl ions to precipitate the magnesium as hydroxide.

**Ionization of Water.** Water is a weak electrolyte with an ion product of  $1.0 \times 10^{-14}$  at  $25^\circ$ , dissociating according to the reaction



The ion product of water has been carefully determined by four different methods, all of which are in excellent agreement.

*Example 5.* Calculate the degree of dissociation and the ion product of water at 25° from the fact that the specific conductance of the purest water has been found to be  $5.5 \times 10^{-8}$  \*mho. The ionic conductances at infinite dilution are  $l_{H^+} = 349.8$  and  $l_{OH^-} = 198$ .

In pure water 18 ml. contains 1 gram-equivalent of  $H_2O$ . Then the equivalent conductance  $\Lambda$  is given by the relation

$$\Lambda = LV = 5.5 \times 10^{-8} \times 18 = 9.9 \times 10^{-7}$$

$$\Lambda_0 = l_c + l_a = 349.8 + 198 = 547.8$$

$$\alpha = \frac{\Lambda}{\Lambda_0} = \frac{9.9 \times 10^{-7}}{547.8} = 1.81 \times 10^{-9}$$

The value 547.8 is the equivalent conductance of a hypothetical, completely ionized water.

Since there are 1000/18 or 55.5 moles of water per liter,

$$c_{H^+} = c_{OH^-} = 55.5\alpha = 55.5 \times 1.81 \times 10^{-9} = 1.00 \times 10^{-7}$$

$$K = \frac{c_{H^+} \times c_{OH^-}}{c_{H_2O}} = \frac{(1.00 \times 10^{-7})^2}{55.5} = 1.8 \times 10^{-16}$$

Since the concentration of water in the denominator remains constant it is usually absorbed into the ionization constant and the ion product  $K_w$  is usually used, as defined thus:

$$K_w = c_{H^+} \times c_{OH^-} = 1.00 \times 10^{-7} \times 1.00 \times 10^{-7} = 1.00 \times 10^{-14}$$

*Example 6.* Determine the ionic product of water from measurements of the hydrogen electrode (page 448) in acid and alkaline solutions. The voltage of the following cell was found to be 0.6560 volt at 25°.†

Pt,  $H_2$ ; 0.1 *M* KOH, 0.1 *M* KCl, 0.1 *M* HCl;  $H_2$ , Pt.

$$a_{H^+} = a_1$$

$$a_{H^+} = a_2$$

The calculated junction potential between 0.1 *M* KOH and 0.1 *M* KCl is -0.0157 and that between 0.1 *M* KCl and 0.1 *M* HCl is -0.0278 volt. Hence the true voltage of the cell without liquid junctions would be 0.6995 volt

$$E = 0.6995 = -0.0591 \log \frac{a_1}{a_2}$$

$$\frac{a_1}{a_2} = 1.50 \times 10^{-12}$$

The activity coefficient of 0.1 *M* HCl is 0.796 and the activity of hydrogen ion,  $a_2$ , is then 0.0796. Then in the potassium hydroxide solution

$$a_{H^+} = 1.50 \times 10^{-12} \times 0.0796 = 1.20 \times 10^{-13}$$

\* Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 317 (1894); Jones and Bradshaw, *J. Am. Chem. Soc.*, **55**, 1800 (1933).

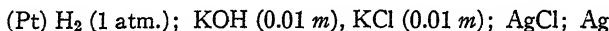
† Lorenz and Böhi, *Z. physik. Chem.*, **66**, 739 (1909).



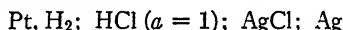
The activity coefficient of 0.1 *M* KOH is 0.772 and  $a_{\text{OH}^-} = 0.0772$ . Then  $K_w = a_{\text{H}^+} \times a_{\text{OH}^-} = 0.0772 \times 1.20 \times 10^{-13} = 0.93 \times 10^{-14}$ . In pure water

$$a_{\text{H}^+} = a_{\text{OH}^-} = \sqrt{K} = \sqrt{0.93 \times 10^{-14}} = 0.96 \times 10^{-7}$$

*Example 7.* Determine the ion product of water at 25° from the following data. The electromotive force of the following cell at 25° is 1.05033 volt.\*



The standard electrode potential  $E^0$  for the cell



is 0.22239 volt at 25°.†

$$K_w = \gamma_{\text{H}^+} c_{\text{H}^+} \gamma_{\text{OH}^-} c_{\text{OH}^-}$$

The cell reaction in both cases is  $\frac{1}{2} \text{H}_2 + \text{AgCl} = \text{H}^+ + \text{Cl}^- + \text{Ag}$ . Hence

$$\begin{aligned} 1.05033 &= 0.22239 - \frac{RT}{nF} \ln \gamma_{\text{H}^+} c_{\text{H}^+} \times \gamma_{\text{Cl}^-} c_{\text{Cl}^-} \\ &= 0.22239 - \frac{RT}{nF} \ln \left[ K_w \times \frac{\gamma_{\text{Cl}^-} c_{\text{Cl}^-}}{\gamma_{\text{OH}^-} c_{\text{OH}^-}} \right] \\ &= 0.22239 - 0.05915 \log \left[ K_w \times \frac{\gamma_{\text{Cl}^-} \times 0.01}{\gamma_{\text{OH}^-} \times 0.01} \right] \end{aligned}$$

In this dilute solution,  $\gamma_{\text{Cl}^-} = \gamma_{\text{OH}^-}$  very closely, although it is not accurate enough to assume that they equal unity. Hence,

$$\begin{aligned} \log K_w &= \frac{-1.05033 + 0.22239}{0.05915} = -13.997 = \overline{14}.003 \\ K_w &= 1.01 \times 10^{-14} \end{aligned}$$

This method has the advantage of involving no uncertain liquid junction potential such as in the preceding example.

Direct determinations of the ion product of water have been made also by measuring the catalytic effects of  $\text{H}^+$  and  $\text{OH}^-$  on the rates of certain organic reactions.

Another method involves the measurement of the hydrolysis of salts as illustrated later in example 11.

The ionization of water is given at various temperatures in Table VII.

The correctness of the data of Table VII figures can be checked further by taking the values of the degree of ionization of water at

\* Harned and Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).

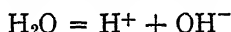
TABLE VII  
HYDROGEN-ION CONCENTRATION OF PURE WATER<sup>1</sup>

$c_{H^+} = c_{OH^-}$  expressed in gram-ions per liter  $\times 10^7$

Temperature	0°	18°	25°	50°
$c_{H^+}$	0.34	0.77	1.01	2.35

<sup>1</sup> International Critical Tables, Vol. VI, p. 152.

two temperatures and calculating the heat of the reaction

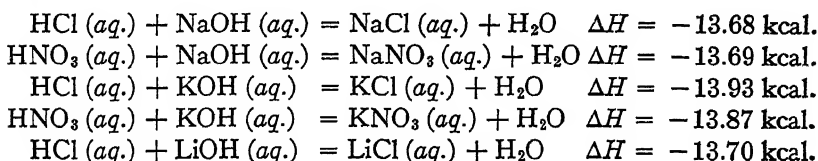


by means of the approximate formula. Thus, from Table VII, the ionic product of water  $K_w$  is  $(0.34 \times 10^{-7})^2$ , at 0°, and  $(2.35 \times 10^{-7})^2$ , at 50°. Introducing these values into the equation

$$\Delta H = \frac{2.3026R(\log K_2 - \log K_1)T_2T_1}{T_2 - T_1}$$

and solving for  $\Delta H$  we obtain +13,500 calories. This value agrees well with that found for the reverse reaction by the direct measurement of the heat of neutralization of completely ionized acids and bases, viz., -13,800 calories as described in the following section.

**Heat of Ionization.** Hess discovered in 1840 that when equivalent quantities of strong acids and bases are mixed in dilute solutions practically the same amount of heat is evolved in each. The following energy equations may be considered as typical examples of such neutralizations at room temperatures:



This constancy in the heat of neutralization of strong acids and bases is easily explained by the ionization theory. The only reaction taking place is that between hydrogen and hydroxyl ions and this occurs in every neutralization. Thus in a neutralization of a strong base  $MOH$  with a strong acid  $HA$  the reactants are completely ionized and the reaction is

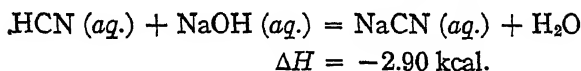
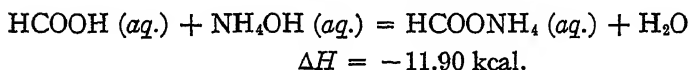
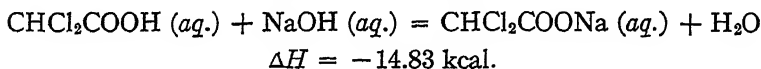
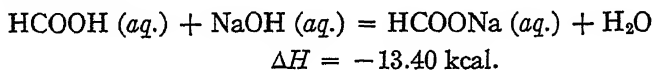


Disregarding the ions which occur on both sides of the equation



Strictly speaking the ions are hydrated, for example  $(\text{H}_3\text{O})^+ \cdot x\text{H}_2\text{O}$  and  $\text{OH}^- \cdot y\text{H}_2\text{O}$ . It thus appears that the neutralization of a strong acid by a strong base in dilute solution consists in the combination of hydrated hydrogen and hydroxyl ions to form undissociated water. The heat of this ionic reaction is  $-13.8$  kg.-cal. The heat of formation of water from its hydrated ions must not be confused with the heat of formation of water from its elements, nor with the heat of combination of the unhydrated ions.

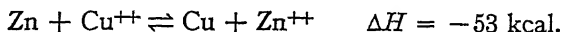
When weak acids or weak bases are neutralized by strong bases or strong acids, respectively, or when weak acids are neutralized by weak bases, the heat of neutralization may differ widely from  $-13.8$  kcal. For example:



As will be seen, the heat of neutralization may be either greater or less than  $13.8$  kcal. The exceptions to the rule that the heat of neutralization of an acid by a base is constant are readily explained by the theory of electrolytic dissociation. The neutralization process involves not only the union of the hydrogen and hydroxyl ions but also the dissociation of a weak acid or a weak base. For example, in the last example given the neutralization of the weak hydrocyanic acid evolves  $2.9$  kcal., whereas  $13.8$  kcal. would be evolved if the acid were completely ionized. The difference,  $10.9$  kcal., then represents the heat absorbed in ionizing hydrocyanic acid in water.

The heat of neutralization is different in concentrated solutions by an amount equal to the heat of dilution. It changes with the temperature by an amount determined by the difference between the heat capacity of the acid and base solution and the heat capacity of the resulting salt solution.

Heats of ionic reactions including neutralizations are determined simply in a calorimeter. When zinc deposits copper from a copper sulfate solution, for example,



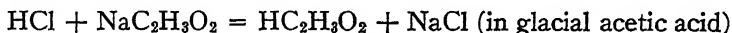
When dilute solutions of ions are mixed, there is no thermal change unless a reaction takes place. For example, when dilute solutions of sodium bromide and sodium nitrate are mixed, no heat is evolved or absorbed. However, when sodium bromide and silver nitrate are mixed there is an evolution of 20 kcal. per mole due to the heat of precipitation of silver bromide. Moreover, in dilute solutions the heat of precipitation of silver bromide is the same at the same temperature whether or not the starting materials were potassium bromide and silver sulfate or any other bromide and silver salts.

It is possible to prepare a table of heats of formation of the different positive and negative ions from which heats of ionic reactions can be calculated. The heat of the reaction  $\frac{1}{2}\text{H}_2 = \text{H}^+ + e$  is usually taken arbitrarily as zero and the heats of formation of other ions are then obtained by difference from known ionic reactions.

**Proton Theory of Acids.** Certain general aspects of the behavior of acids and bases were overlooked, because of the importance of water and its solutions, and because of the successes of the Arrhenius theory. Thus, according to an older viewpoint, only aqueous solutions show acid and basic properties, and the term neutralization refers to the combination of hydrogen ions and hydroxyl ions. But the formation of water is not a necessary criterion for neutralization. For example, the following reactions



and



give the usual neutralization curve with electrometric titration.

Since 1923, under the leadership of Brønsted and Bjerrum in Denmark, as well as Lowry in England, and others, the proton theory of acids and bases has been gaining ground.\* According to this view acids and bases are uniquely characterized by a tendency to exchange protons, i.e., hydrogen ions, just as oxidizing and reducing agents are uniquely characterized by a tendency to exchange electrons. There is much in common between these two systems. For example, a given material may be a reducing agent with respect to another one which is lower in the electromotive series, but it may be an oxidizing agent toward a substance higher in the series. In the same way a

\* Hall, *J. Chem. Education*, **7**, 782 (1930).

A complete discussion of the theory of acids is given in "Contributions to Chemical Education 1," entitled "Acids and Bases," *J. Chem. Education*, Easton, Pa., 1941. A bibliography is given by Alyea, *J. Chem. Education*, **16**, 535 (1939).

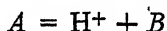
given substance may be an acid with respect to a substance of greater base strength, or it may act as a base toward a substance of lesser base strength.

According to this very simple view *an acid is a substance which has a measurable tendency to give up protons* ( $H^+$  ions). Thus any compound which contains hydrogen may conceivably act as an acid, but in methane and in hydride ion ( $H^-$ ) and similar compounds, the tendency to give protons is so extremely small (i.e., the force holding the proton is so great) that the substances can hardly be classed as acids.

The *strength of an acid* is the quantitative measure of its tendency to release protons. It varies with the solvent and the experimental conditions and is determined by the electronic and nuclear structure of the acid. Thus HI is intrinsically a stronger acid than HF because its internuclear distance is greater and the proton is held less firmly, and  $HMnO_4^-$  is intrinsically weaker than  $HMnO_4$  because the negative charge tends to prevent the escape of the positive proton.

An uncharged acid cannot of itself separate into a positive proton and negative anion; energy must be supplied from somewhere. This energy may come from a chemical reaction such as the combination between the proton and the solvent.

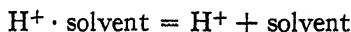
According to the simplest view an acid  $A$  dissociates as follows,



where  $B$  is a *base*, defined by Brönsted as a substance which takes up protons; but according to a more nearly complete picture, it is necessary to include something to react further with the free proton, providing energy for the liberation of the proton from the acid. Thus,



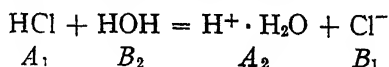
But since



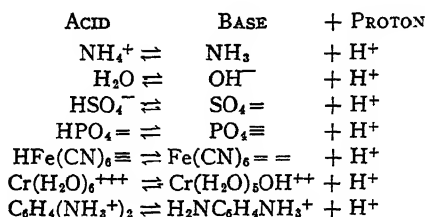
$H^+ \cdot \text{solvent}$  may be regarded as an acid  $A_2$  and the solvent as a base  $B_2$ . Then rewriting equation (7)



Hydrochloric acid in water may be taken as a specific example.



This system emphasizes the similarity between all such processes as the following:



All these reactions take place in water solution to an easily measurable extent because water acts as a *base* and forms the hydrated proton. The hydrated proton is often called the hydronium ion ( $\text{H}_3\text{O}^+$ ). The extent to which these reactions run in different solvents depends on the base strength of the solvent, i.e., the ability of the solvent to attach protons. Thus at equal concentrations all the dissociations would be very complete in the solvent liquid ammonia, and very incomplete in the solvent acetic acid. The solvent ammonia has a much greater attraction for protons than has the solvent acetic acid.

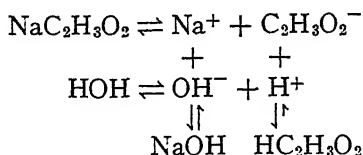
Dissociation of a dissolved acid into protons occurs by combination with the solvent, and the result of this solvolysis is to diminish the acidity since a weaker acid is always formed by interaction with the solvent. According to this view HCl is actually very acid in benzene in which the solvation of the proton is slight, less acid in water in which it is more solvated, and still less acid in ammonia in which the union of the proton with the solvent must be still more complete.

A still more general theory of acids has been proposed by G. N. Lewis\* who points out that substances like  $\text{SO}_3$  and  $\text{CO}_2$  behave as acids although they contain no hydrogen. He suggests that an acid is a molecule, radical, or ion which can accept an electron pair from some other atom to complete its stable quota of electrons, usually an octet. A base is a substance which can share this electron pair with an acid. In other words an acid is an electron "acceptor" and a base is an electron "donor." This definition covers all the acids included in the proton theory of acids and many additional ions also. The fact that this concept is more general makes it less definite in describing the properties of specific acids and bases.

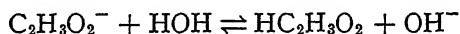
**Hydrolysis.** When a salt formed by a weak acid and a strong base, such as sodium acetate, is dissolved in water, the solution shows an

\* Luder, "The Electronic Theory of Acids and Bases," *Chem. Rev.*, **27**, 547 (1940)

alkaline reaction because some of the hydrogen ions from the water are bound up in the undissociated acetic acid, leaving an excess of hydroxyl ions. Thus



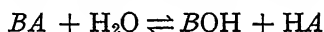
The sodium acetate and the sodium hydroxide are highly ionized. More and more of the water dissociates to supply hydrogen ions for the production of acetic acid molecules. Finally an equilibrium is reached at which there is a definite ratio of  $\text{H}^+$  ions to  $\text{OH}^-$  ions. The situation is more simply described by stating that the acetate ions have a greater attraction for protons than the hydroxyl ions. Thus



Ammonium chloride hydrolyzes in water to give an acid reaction because some of the hydroxyl ions from the water are removed as ammonium hydroxide, leaving an excess of hydrogen ions.

Ferric chloride hydrolyzes to give an acid reaction because the hydroxyl ions are removed by the formation of ferric hydroxide, which is very insoluble.

In general the reaction between a dissolved salt and the water is called *hydrolysis*, and the equation may be written



where  $B$  is the basic constituent and  $A$  the acid constituent of the salt  $BA$ . The general term for reaction with any solvent is *solvolysis*.

Hydrolysis is due to the removal of either one, or both, of the ions of water by the ions of the salt, to form undissociated or insoluble substances. As fast as the ions of water are removed, the loss is made good by the dissociation of more water until, eventually, a condition of equilibrium is established. The conditions governing hydrolytic equilibrium may be determined from a knowledge of the solubilities and ionization constants of the substances involved.

Any method which gives the effective concentration of hydrogen ions in the hydrolyzed solution permits the calculation of the degree of hydrolysis of a salt. When a salt of a weak base and a strong acid hydrolyzes, the base reacts with the hydroxyl ions of the water but the acid is completely ionized. Each hydrogen ion produced then corresponds to the hydrolysis of an equivalent amount of the salt.

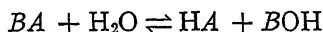
*Example 8.* When 1 mole of ammonium chloride is dissolved in 32 liters of water at 25° and allowed to reach equilibrium, a hydrogen electrode in the solution registers 0.605 volt against the normal calomel electrode. Calculate the degree of hydrolysis.

$$\mu H = \frac{0.605 - 0.281}{0.059} = 5.48. \quad \text{Therefore } \log c_{H^+} = -5.48 = \bar{5}.52$$

$$c_{H^+} = 3.3 \times 10^{-6}$$

$$c_{H^+} = \frac{x}{v} \quad \text{and} \quad x = 3.3 \times 10^{-6} \times 32 = 1.06 \times 10^{-4}$$

The determination of the degree of hydrolysis of a salt may be determined also by means of electrical conductance. When a salt  $BA$  hydrolyzes as follows:



the limiting value of its equivalent conductance when hydrolysis is complete is  $\Lambda_{HA} + \Lambda_{BOH}$ , where  $\Lambda_{HA}$  and  $\Lambda_{BOH}$  denote the equivalent conductances of the acid and base formed. If  $\Lambda_s$  is the equivalent conductance of the unhydrolyzed salt, and  $\Lambda_h$  is the actual conductance of the partially hydrolyzed salt at the same dilution, then the increase in conductance, corresponding to a degree of hydrolysis,  $x$ , will be  $\Lambda_h - \Lambda_s$ . If the hydrolysis were complete, the increase in equivalent conductance would be  $\Lambda_{HA} + \Lambda_{BOH} - \Lambda_s$ , hence

$$x = \frac{\Lambda_h - \Lambda_s}{\Lambda_{HA} + \Lambda_{BOH} - \Lambda_s} \quad [9]$$

all conductances being measured at the same dilution and at the same temperature. The value of  $\Lambda_s$ , the equivalent conductance of the unhydrolyzed salt, may be found by determining the conductance of the salt in the presence of an excess of one of the products of hydrolysis, and deducting from it the conductance of the substance added. Under these conditions the hydrolysis is rendered negligible.

*Example 9.* The equivalent conductance of an 0.0108  $M$  solution of aniline hydrochloride is 118.6 reciprocal ohms. When an excess of aniline is added (i.e., the solution is saturated with aniline) the equivalent conductance drops to 103.6. The conductance of pure aniline in water is negligible. The equivalent conductance of hydrochloric acid at the same concentration is 426.1. Calculate the degree of hydrolysis  $x$ .

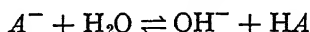
$$x = \frac{\Lambda_h - \Lambda_s}{\Lambda_{HA} + \Lambda_{BOH} - \Lambda_s} = \frac{118.6 - 103.6}{426.1 + 0 - 103.6} = 0.0465$$

**Calculation of Hydrolysis Constants.** There are three types of hydrolysis, involving (a) the salt of a strong base and a weak acid,



(b) the salt of a weak base and a strong acid, and (c) the salt of a weak base and a weak acid.

(a) *Hydrolysis of a Salt of a Strong Base and a Weak Acid.* This type of reaction may be represented by the general equation



The equilibrium constant,  $K$ , of this equation may be written

$$K = \frac{c_{HA} \times c_{OH^-}}{c_{H_2O} \times c_{A^-}} \quad [10]$$

The concentration of water is regarded as constant because water is present in large excess, and the hydrolysis constant  $K_h$  is written

$$K_h = \frac{c_{HA} \times c_{OH^-}}{c_{A^-}} \quad [11]$$

Since the ionization constant of water  $K_w = c_{H^+} \times c_{OH^-}$ , it follows that

$$c_{OH^-} = \frac{K_w}{c_{H^+}}$$

Also the dissociation constant of the acid  $K_a$  is

$$\frac{c_{H^+} \times c_{A^-}}{c_{HA}} = K_a$$

Substituting these values in equation (11),

$$K_h = \frac{K_w}{K_a} \quad [12]$$

The ionization of the salt and the base is practically complete. If the degree of hydrolysis of the salt (i.e., the fraction of the ions which react with water) is designated by  $x$  and the original concentration of the salt by  $c_s$  then

$$c_{HA} = xc_s, \quad c_{OH^-} = xc_s, \quad \text{and} \quad c_{A^-} = (1 - x)c_s$$

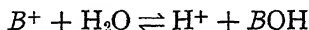
On substituting these values in equation (11), we have

$$K_h = \frac{K_w}{K_a} = \frac{c_s x^2}{(1 - x)} \quad [13]$$

If  $(1 - x)$  differs but little from unity, equation (13) may take the form

$$x = \sqrt{\frac{K_w}{K_a c_s}} \quad [14]$$

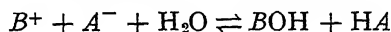
(b) *Hydrolysis of a Salt of a Weak Base and a Strong Acid.* The reaction is represented by the equation



It can be shown in a manner similar to that described under (a) that

$$K_h = \frac{K_w}{K_b} = \frac{c_s x^2}{(1-x)} \quad [15]$$

(c) *Hydrolysis of a Salt of a Weak Base and a Weak Acid.* This type of reaction may be represented by the equation



and the equilibrium constant is given by the equation

$$K = \frac{c_{BOH} \times c_{HA}}{c_{H_2O} \times c_{B^+} \times c_{A^-}} \quad [16]$$

But the dissociation constant of the base is given by the relation,

$$K_b = \frac{c_{B^+} \times c_{OH^-}}{c_{BOH}}, \text{ and } c_{BOH} = \frac{c_{B^+} \times c_{OH^-}}{K_b}$$

and similarly the dissociation constant of the acid is given by the relation

$$K_a = \frac{c_{H^+} \times c_{A^-}}{c_{HA}}, \text{ and } c_{HA} = \frac{c_{H^+} \times c_{A^-}}{K_a}$$

Substituting these values in equation (16), and assuming as before that the concentration of water is constant, the hydrolysis constant is given by the equation

$$K_h = \frac{c_{H^+} \times c_{OH^-}}{K_a \times K_b} = \frac{K_w}{K_a \times K_b} \quad [17]$$

In the special case where the weak acid and base are both dissociated to the same extent,  $c_{HA} = c_{BOH} = xc_s$ , and  $c_{B^+} = c_{A^-} = (1-x)c_s$ . On substituting these values in equations (16) and (17)

$$K_h = \frac{x^2}{(1-x)^2} = \frac{K_w}{K_a K_b} \quad [18]$$

On the assumption that the salt is slightly hydrolyzed and  $(1-x)$  is nearly equal to 1, equation (18) may be written in the form

$$x = \sqrt{\frac{K_w}{K_a K_b}} \quad [19]$$

Salts belonging to the third type give, as a first approximation, a constant degree of hydrolysis which is independent of the dilution.

*Example 10.* Calculate at 25° the degree of hydrolysis and the pH of a 0.1 molar solution of potassium cyanide. This is a salt of a strong base and a weak acid. The values of  $K_{\text{HCN}}$  and  $K_w$  are found in the tables.

$$K_b = \frac{K_w}{K_a} = \frac{c_s x^2}{1-x}$$

$$\frac{1.0 \times 10^{-14}}{7.2 \times 10^{-10}} = \frac{0.1x^2}{1-x}$$

$$x = 0.0123$$

$$c_{\text{OH}^-} = 0.1 \times 0.0123 = 0.00123.$$

Assuming that  $a_{\text{OH}^-} = c_{\text{OH}^-}$

$$p\text{OH} = -\log a_{\text{OH}^-} = -\log 0.00123 = -\bar{3}.09 = 2.91. \therefore pH = 11.09.$$

*Example 11.* Calculate the ion product for water from the fact that a 0.1 molar solution of sodium acetate is 0.0080 per cent hydrolyzed at 25°. The salt as well as the sodium hydroxide formed from its hydrolysis may be considered to be completely ionized. The ionization constant of acetic acid is  $1.8 \times 10^{-5}$ .

$$K_w = K_a \times \frac{c_s x^2}{(1-x)} = 1.8 \times 10^{-5} \times \frac{0.1 \times (0.000080)^2}{(1 - 0.000080)}$$

$$= 1.16 \times 10^{-14}$$

Then

$$c_{\text{H}^+} = c_{\text{OH}^-} = \sqrt{K} = \sqrt{1.16 \times 10^{-14}} = 1.1 \times 10^{-7}$$

Compare this result with that obtained in examples 5, 6, and 7.

**Buffer Solutions.** If a single drop of 0.1 *m* HCl is added to a liter of pure water, an enormous increase in the hydrogen-ion concentration will occur immediately. In like manner, the addition of a drop of 0.1 *m* KOH to a liter of pure water will cause a correspondingly large increase in the hydroxyl-ion concentration. Pure water alone is incapable of neutralizing even traces of acids and bases.

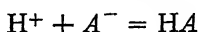
It has been shown that any solution containing a weak acid together with one of its salts, or a weak base with one of its salts, tends to neutralize both acids and bases. This ability of certain solutions to resist change in hydrogen-ion concentration, on the addition of acid or alkali, is known as *buffer action*, and the solutions are called *buffer solutions*.

The explanation of buffer action is simple. If an alkali is added

to a buffer solution containing a weak acid  $HA$  and one of its salts  $MA$ , the alkali is neutralized by the acid, thus



If an acid is added, the hydrogen ions which it contains react with the anions of the salt to form the undissociated weak acid, thus



It follows that, if the reserve acidity is to be equal to the reserve alkalinity, the concentration of  $A^-$  must be equal to the concentration of  $HA$ . Then, if  $K_{HA}$  is the ionization constant of the weak acid of the buffer solution

$$C_{H^+} = \frac{C_{HA}}{C_{A^-}} K_{HA} = K_{HA} \quad [20]$$

In other words, the hydrogen-ion concentration of a buffer solution of this type is numerically equal to the ionization constant of the acid if the concentration of the dissociated salt is equal to the concentration of the undissociated acid (essentially equal to the total concentration of the acid).

Examples of buffer solutions are given in Table VIII.

TABLE VIII  
BUFFER SOLUTIONS

			pH range
Phthalic acid	+	potassium acid phthalate	2.2-3.8
Acetic acid	+	sodium acetate	3.5-5.5
Citric acid	+	disodium phosphate	2.4-8.0
Boric acid	+	sodium borate	7.0-9.1
Disodium phosphate	+	trisodium phosphate	11.0-12.0

Slight changes in the ratio of acid to salt permit the alteration in  $pH$  by small amounts. For example, a 20-ml. mixture of 0.2  $m$   $Na_2HPO_4$  and 0.1  $m$  citric acid can be given a  $pH$  ranging from 2 to 8 by changing the ratio as shown in Table IX.

TABLE IX  
PHOSPHATE-CITRIC ACID BUFFERS

ml. 0.2 $m$ $Na_2HPO_4$	3.17	4.11	7.71	10 30	12.63	16 47	19.45
ml. 0.1 $m$ Citric acid	16.83	15.89	12.29	9 70	7.37	3.53	0.55
$pH$	2.8	3	4	5	6	7	8

Because buffer solutions can be made to change  $pH$  so gradually they are widely used in determining colors of indicators. Slight grada-

tions in color are brought out which are missed in the titration of an unbuffered solution. A few typical indicators suitable for different  $pH$  ranges are given in Table X.

TABLE X

## INDICATORS

Indicator	$pH$ range	Indicator	$pH$ range
Picric acid	0 0-1 3	Brom thymol blue	6 0- 7.6
Thymol blue	1 2-2 8	Phenol red	7 2- 8 8
Brom phenol blue	3 0-4 6	Thymol blue	8 2- 9 8
Methyl orange	3 1-4 4	Phenolphthalein	8 3-10 0
Methyl red	4 4-6 0	Alizarine yellow R	10 1-12 1
Brom cresol purple	5 4-7.0	Nitramine	11.0-13 0

Buffer solutions are widely used as standards in color titrations when it is desired to titrate to a definite  $pH$  value. The  $pH$  of a given solution may often be determined by introducing the proper indicator and comparing the color with the colors obtained by adding the indicator, such for example as phenolphthalein, to a series of buffer solutions. The  $pH$  of the solution is the same as that of the particular buffer whose color matches. Tables of suitable indicators have been arranged which cover the whole range of  $pH$  values.

Buffer solutions are important in analytical chemistry, in general laboratory work and particularly in biochemistry, where it is desired to keep the number of variables to a minimum. Blood, milk, and various animal fluids are highly buffered with bicarbonate ions and carbonic acid, and with other protein systems. The  $pH$  of human blood in a normal person is approximately 7.4. Ordinarily variations are less than 0.1 of a  $pH$  unit and an increase or decrease of as much as 0.4 is likely to be fatal.

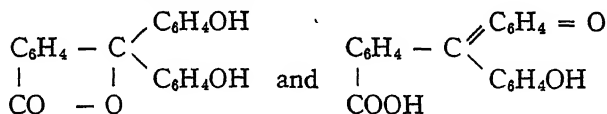
Different enzymes have certain optimum  $pH$  values which must be rather closely maintained. The type of plants growing in a certain locality is largely influenced by the  $pH$  of the soil. Forest soil with decaying leaves is likely to be acid, whereas limestone soil will have a higher  $pH$ . For proper productivity of crops it is often necessary to add limestone (or sulfur, which changes to sulfuric acid) to give the proper  $pH$  to the soil.

**Theory of Indicators.\*** An indicator is a weak acid which changes in certain  $pH$  ranges when acids or bases are added. The weak

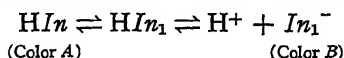
\* A complete discussion of this subject is given by Kolthoff (translation by Rosenblum), "Acid-Base Indicators," The Macmillan Co., 1937.

indicator acid competes with strong acid for the added base and only after the strong acid is neutralized is it affected. When a solution of a base is titrated with an acid, the end point is reached when the amount of acid added is just equivalent to the amount of base present. Theoretically, the solution at the end of the titration should be identical in composition with a solution prepared by dissolving a known weight of the salt formed in the process of neutralization, in the calculated amount of the solvent. However, the salt may be hydrolyzed and, therefore, the indicator should not necessarily change its color at exact neutrality but rather it should change its color when the hydrogen-ion concentration of the solution acquires the same value as that which exists in a solution of the salt formed by adding equivalent quantities of acid and base.

In order to understand the mechanism of the action of indicators, it must be remembered that almost all indicators are weak organic acids which are capable of existing in two tautomeric forms in equilibrium with each other. For example, phenolphthalein has been shown to exist in the two following forms:



One of these forms, which for convenience we may designate by the formula  $\text{HIn}$ , is a nonelectrolyte, while the other form, which may be represented by the formula  $\text{HIn}_1$ , is an electrolyte and, as such, is ionized in solution. The equilibria existing in a solution of such an indicator acid may be represented in the following manner:



The criteria of a good indicator are that there shall be a sharp contrast between the two colors which it exhibits in acid and alkaline media, and that the value of the ratio  $\text{HIn}_1/\text{HIn}$  shall be small. It is apparent that the addition of a strong acid to a solution containing an indicator-acid will displace the above equilibria toward the left, with the production of the so-called "acid color" of the indicator. In like manner, the addition of a base to the solution of an indicator-acid will displace the equilibria toward the right, with the development of the so-called "alkaline color" of the indicator. The "neutral color" of an indicator is intermediate between the acid and alkaline colors, and is obtained when the concentration of the hydrogen ion in the solution assumes a value such that one-half of the indicator is in the form  $\text{HIn}$  and the

other half is in the form  $In_1^-$ . One of the "colors" may be lacking as in the acid color of phenolphthalein.

According to the law of mass action,

$$\frac{c_{H^+} \times c_{In_1^-}}{c_{HIn}} = K_{HIn}$$

or

$$c_{H^+} = K_{HIn} \frac{c_{HIn}}{c_{In^-}} \quad [21]$$

If the effective concentrations of the indicator in the molecular form and in the ionized form are equal when the indicator exhibits its neutral color

$$\frac{c_{HIn}}{c_{In^-}} = 1$$

and

$$c_{H^+} = K_{HIn} \quad [22]$$

With most indicators it is difficult to detect a sharp color change over a narrow range of  $pH$ . Often it is possible to neutralize about 10 per cent of the indicator before a change in color is detectable and the change does not appear to be complete until about 90 per cent of the indicator is neutralized. Then the visible range of color change gives values of  $c_{HIn}/c_{In^-}$  from 0.9/0.1 to 0.1/0.9. This corresponds roughly to a  $pH$  range of 2.

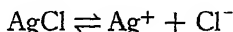
The exact ratio of  $c_{HIn}/c_{In^-}$  can be determined experimentally by measuring the milliliters of base which must be added to a known amount of indicator to bring about a detectable color change.

Color indicators may be used not only to show when a certain hydrogen-ion concentration is reached but also to show when a certain ratio of oxidizing to reducing material is reached. In the former case the color change corresponds to a definite voltage of the hydrogen electrode whereas the latter corresponds to a definite voltage of an inert platinum electrode. The loss of color by the reduction of potassium permanganate is well known. The reaction takes place at a definite reduction-oxidation potential. Certain organic compounds such as diphenylbenzidine change color sharply at a given reduction potential and  $pH$ . By having a series of these reduction-oxidation indicators and noting which one changes color when placed in a solution, the reduction-oxidation potential of the solution may be readily determined.

Products from some bacterial actions have reducing action and can be tested for, by changing the color of a reduction-oxidation indicator.

For example, milk that has been subjected to bacterial action will decolorize methylene blue.

**The Solubility Product.** A saturated solution of silver chloride is practically completely ionized, as represented by the equation



Applying the law of mass action to this equilibrium,

$$\frac{a_{\text{Ag}^+} \times a_{\text{Cl}^-}}{a_{\text{AgCl}}} = K$$

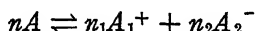
The activity of a solid may be considered equal to unity, and so  $a_{\text{AgCl}}$  need not be considered in the formula. Substituting concentrations in moles per liter for activities, the approximate equation (23) is obtained, thus

$$c_{\text{Ag}^+} \times c_{\text{Cl}^-} = K a_{\text{AgCl}} = s \quad [23]$$

in which the product of the ionic concentrations,  $s$ , is called the *solubility product*.

The solubility of silver chloride in pure water, at  $25^\circ$ , is  $1.25 \times 10^{-5}$  mole per liter and, since the dissociation is complete, there must be  $1.25 \times 10^{-5}$  gram-ion of  $\text{Ag}^+$  and  $1.25 \times 10^{-5}$  gram-ion of  $\text{Cl}^-$  per liter. The solubility product  $s$  is therefore  $(1.25 \times 10^{-5})^2$ , or  $1.56 \times 10^{-10}$ .

In general, if



represents the equilibrium between an electrolyte and its products of dissociation in saturated solution,

$$c^{n_1} A_1^+ \times c^{n_2} A_2^- = s \quad [24]$$

The *solubility product* may be defined as the maximum product of the ionic concentrations of an electrolyte which can exist in equilibrium with the undissolved phase at any one temperature, each concentration being raised to its proper exponent.

The following example will serve to illustrate how the solubility product of a substance can be determined, and how the change in solubility, due to the addition of a substance containing a common ion, may be calculated.

**Example 12.** The solubility of strontium oxalate at  $20^\circ$  is 0.00054 mole per liter. Calculate the solubility product.

$$s = c_{\text{Sr}^{++}} c_{\text{C}_2\text{O}_4^{--}} = (0.00054)(0.00054) = 2.915 \times 10^{-7}$$



How much strontium oxalate will be dissolved in a solution of 0.04 *M* sodium oxalate. Let *x* equal the moles of strontium oxalate which dissolve per liter.

$$s = 2.915 \times 10^{-7} = c_{\text{Sr}^{++}} + c_{\text{C}_2\text{O}_4^{--}} = x(x + 0.04) = x^2 + 0.04x$$

$$x = 7.3 \times 10^{-6} \text{ mole}$$

( $x^2$  is so small in this example that it may be dropped out in solving this equation)

*Example 13.* Calculate the solubility product of silver chromate if the solubility is  $8 \times 10^{-5}$  mole per liter.

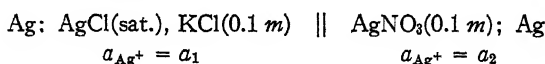
$$s = c_{\text{Ag}^+}^2 c_{\text{CrO}_4^{--}} = (0.00016)^2 (0.00008) = 2 \times 10^{-12}$$

A few solubility products are given in Table XI.

TABLE XI  
SOLUBILITY PRODUCTS AT 25°

AgCl	$1.2 \times 10^{-10}$	Mg(OH) <sub>2</sub>	$2 \times 10^{-11}$
AgBr	$7.7 \times 10^{-13}$	CaC <sub>2</sub> O <sub>4</sub>	$2.6 \times 10^{-9}$
AgI	$0.9 \times 10^{-16}$	CaCO <sub>3</sub>	$9.3 \times 10^{-8}$
CaSO <sub>4</sub>	$6.2 \times 10^{-5}$	PbS	$1 \times 10^{-28}$
SrSO <sub>4</sub>	$2.8 \times 10^{-7}$	MnS	$1.4 \times 10^{-15}$
BaSO <sub>4</sub>	$1.1 \times 10^{-10}$	Ag <sub>2</sub> S	$1.6 \times 10^{-49}$
PbSO <sub>4</sub>	$1.0 \times 10^{-8}$		

*Example 14.* Determine the solubility of silver chloride by means of a silver electrode, described on page 427. The voltage *E* for the following cell was found to be 0.4550 volt at 25°.



The activity coefficient of 0.1 *m* AgNO<sub>3</sub> is 0.82. Calculating the activity of silver ions in the saturated silver chloride solution at the left

$$E = 0.4550 = -0.0591 \log \frac{a_1}{a_2} = -0.0591 \log \frac{a_1}{0.82 \times 0.1}$$

$$a_1 = 1.67 \times 10^{-9}$$

The activity coefficient of 0.1 *m* KCl is 0.76 and it is not appreciably changed by the very small amount of silver chloride dissolved. Then

$$a_{\text{Ag}^+} \times a_{\text{Cl}^-} = (1.67 \times 10^{-9}) \times (0.76 \times 0.1) = 1.27 \times 10^{-10}$$

When silver chloride is dissolved in pure water the concentrations of silver and chloride ions are equal. Moreover the solution is so dilute that the activities are the same as the concentrations. Then

$$\text{Solubility} = \sqrt{c_{\text{Ag}^+} \times c_{\text{Cl}^-}} \cong \sqrt{a_{\text{Ag}^+} \times a_{\text{Cl}^-}} = \sqrt{1.27 \times 10^{-10}}$$

$$= 1.13 \times 10^{-5} \text{ mole of silver chloride per 1000 g. of water}$$

**Strong Electrolytes.** Thus far this chapter has dealt mostly with weak electrolytes, which exist largely in the form of undissociated or un-ionized molecules. They include many organic acids and bases and a few inorganic compounds. The strong electrolytes, which include almost all salts, the mineral acids like hydrochloric and sulfuric, and the alkali hydroxides, will now be discussed.

Several properties of these strong electrolytes have been studied in earlier chapters — the effective concentration of the dissociated ions as determined by electromotive force measurements, the abnormal lowering of the freezing point, and the change of equivalent conductance with dilution.

The physical properties of completely ionized solutions are, in general, additive. For example, the permanganates of lithium, cadmium, ammonium, zinc, potassium, sodium, magnesium, hydrogen, and aluminum give absorption spectra which are practically identical. Since the permanganate ion is colored, and common to all the salts examined, and the positive ions of the various substances are colorless, it follows that, when dissociation is complete, the absorption spectra of all the solutions should be identical. It has been shown already that the equivalent conductance at infinite dilution is equal to the sum of the ionic conductances. The heats of ionic reactions also can be calculated by adding the heats of formation of all the ions of the reactants and the products and subtracting the latter from the former.

**Classification of Electrolytes.** In addition to the distinction between weak electrolytes and strong electrolytes, another sub-classification of the strong electrolytes based on valences is useful. Electrolytes such as NaCl, KCl, KOH, and HCl which yield on dissociation two singly charged ions are called uni-univalent electrolytes, while such substances as  $\text{CuSO}_4$  and  $\text{MgSO}_4$  are called bi-bivalent electrolytes. In the same way,  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{CO}_3$  are uni-bivalent,  $\text{Ca}(\text{OH})_2$  and  $\text{BaCl}_2$  are bi-univalent, and  $\text{K}_3\text{Fe}(\text{CN})_6$  is uni-trivalent.

The total number of ions,  $\nu$ , is important, in determining the factor by which the freezing-point depression or other property must be multiplied in very dilute solutions. For NaCl,  $\nu = 2$ ; for  $\text{CuSO}_4$ ,  $\nu = 2$ ; for  $\text{BaCl}_2$ ,  $\nu = 3$ ; for  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  $\nu = 4$ ; etc. In more concentrated solutions the multiplication factors are smaller than these numbers, as shown on page 224, because the attraction between ions becomes greater as the number of charges on an ion increases. It is to be expected, then, that the high-valence types will deviate more from the values obtained at infinite dilution than will the uni-univalent electrolytes — a fact which is fully verified by experiment.

The charges on the ions can be treated most successfully in terms of

the *ionic strength*, a term which was first used by G. N. Lewis.\* In calculating the ionic strength,  $\mu$ , of a strong electrolyte the concentration of each ion (in gram-ions per 1000 g. of solvent) is multiplied by the square of its valence and all these quantities are added together and divided by 2.† The factor 2 is included because both positive and negative ions are involved.

*Example 15.* Calculate the ionic strength of the following solutions of electrolytes.

$$\text{For } 0.01 \text{ } m \text{ NaCl, } \mu = \frac{0.01 \times 1^2 + 0.01 \times 1^2}{2} = 0.01$$

$$\text{For } 0.01 \text{ } m \text{ CuSO}_4, \mu = \frac{0.01 \times 2^2 + 0.01 \times 2^2}{2} = 0.04$$

$$\text{For } 0.01 \text{ } m \text{ H}_2\text{SO}_4, \mu = \frac{0.01 \times 1^2 + 0.01 \times 1^2 + 0.01 \times 2^2}{2} = 0.03$$

Several properties of electrolytes depend not on the specific property of the electrolyte but merely on the ionic strength. For example, the influence of an inert electrolyte on the solubility of a difficultly soluble salt is a function of the ionic strength. There is little difference in the effect on the solubility of thallos bromide by sodium chloride, potassium nitrate, and lithium acetate. Since they are all uni-univalent electrolytes they will have the same ionic strength at the same concentration. Moreover since the ionic strength of copper sulfate is four times as great as that for a uni-univalent electrolyte, nearly the same effect on the solubility will be produced by copper sulfate as by sodium chloride at one-fourth the concentration.

Again, for strong electrolytes the ionic strength determines to a large extent the influence of concentration on the deviation from the behavior of ideal solutions. The quantitative deviations are shown in Table XII.

The ratio  $i$  was shown on page 224 to be the ratio of the freezing-point lowering of a given solute to the freezing-point lowering of an ideal nonelectrolyte. Thus  $i = (\Delta T_f/m)/1.855$ . As the solution approaches infinite dilution,  $i$  approaches  $\nu$ , where  $\nu$  is the number of ions (1, 2, or 3, etc.) into which the electrolyte dissociates. (Table V, page 224.)

The ratio  $i/\nu$  then is 1 at infinite dilution, and it becomes less than

\* Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 373.

† Sometimes concentrations on a volume basis rather than a weight basis are used, particularly in applications of the Debye-Hückel theory.

TABLE XII

INFLUENCE OF IONIC STRENGTH ON BEHAVIOR OF STRONG ELECTROLYTES

Electrolyte	Molality	Ionic Strength	Molal Freezing-Point Depression	$i = \frac{\Delta T_f/m}{1.855}$	$\frac{i}{\nu}$
KCl	0.01	0.01	3.610	1.943	0.97
AgNO <sub>3</sub>	0.01	0.01	3.60	1.94	0.97
CuSO <sub>4</sub>	0.01	0.04	2.703	1.45	0.73
ZnSO <sub>4</sub>	0.01	0.04	2.80	1.51	0.76
K <sub>2</sub> SO <sub>4</sub>	0.01	0.03	5.198	2.80	0.93
LaCl <sub>3</sub>	0.01	0.06	8.0	4.3	1.0
K <sub>3</sub> Fe(CN) <sub>6</sub>	0.01	0.06	6.966	3.75	0.94
K <sub>4</sub> Fe(CN) <sub>6</sub>	0.01	0.10	6.8	3.66	0.73
KCl	0.05	0.05	3.50	1.88	0.94
K <sub>2</sub> SO <sub>4</sub>	0.0167	0.05	5.02	2.70	0.90
CuSO <sub>4</sub>	0.0125	0.05	2.66	1.43	0.72
LaCl <sub>3</sub>	0.0083	0.05	6.6	3.55	0.89
K <sub>3</sub> Fe(CN) <sub>6</sub>	0.0083	0.05	6.75	3.63	0.91
K <sub>4</sub> Fe(CN) <sub>6</sub>	0.0050	0.05	7.1	3.8	0.76

unity in more concentrated solutions as the charged ions collide more frequently and cause a departure from the behavior of an ideal solution. The point to be observed in the table is that for salts of a given valence type the magnitude of this ratio  $i/\nu$  depends primarily on the ionic strength. At a given concentration all uni-univalent electrolytes have a definite value of  $i/\nu$  regardless of the chemical nature of the salt, and uni-bivalent electrolytes and bi-bivalent electrolytes have other definite values depending on the ionic strength.

The ionic strength, then, is more fundamental than the chemical nature of the electrolyte or the concentration in predicting how the properties of solutions of strong electrolytes will differ from the properties at infinite dilution. These relations apply also to weak electrolytes, but then the much greater effect of partial ionization makes them relatively unimportant. For weak electrolytes  $i/\nu$  may be used to calculate the degree of dissociation. But for strong electrolytes  $i/\nu$  differs from unity solely because of interionic attraction and it does not give the degree of dissociation, which is practically unity.

**Interionic Attraction.** The behavior of strong electrolytes in moderate concentrations can be understood in a qualitative way by realizing that oppositely charged ions attract each other and cause deviations from the behavior of ideal solutions just as the attraction between molecules in a gas causes deviations from the behavior of

an ideal gas. The quantitative aspects of the theory have been developed by Debye and Hückel as will be shown later. The positive and negative ions are so far apart in very dilute solutions that they exert no attractions on each other and the molal freezing-point depression or other osmotic property is just twice as much for a univalent electrolyte like potassium chloride as it is for a nonelectrolyte like sugar. According to one view, the addition of nonvolatile ions to water decreases the rate at which the water molecules can leave the surface and thus reduces the vapor pressure of the water. However, when the solution is at all concentrated the interionic attraction tends to pull the ions inward away from the surface thus making the effect per ion less. The magnitude of this interionic attraction depends not only on the concentration but also on the valence type; a divalent ion with its two charges exerts a greater interionic attraction than a univalent ion. These two influences find quantitative expression in the ionic strength as described in the preceding section.

It might be thought that there is no essential difference between these partially attracted ions of the interionic attraction theory and the undissociated molecules of the Arrhenius theory. For weak electrolytes the Arrhenius theory is adequate but for strong electrolytes it offers no explanation of the important effect of valence type and ionic strength. Moreover the experimental evidence, such as the ionic nature of the crystal lattice, supports the view that most strong electrolytes are practically completely dissociated into ions.

The quantity  $i/\nu$ , given in Table XII, is known as the osmotic coefficient,  $g$ . When the solution of the strong electrolyte is at infinite dilution  $i/\nu$  becomes 1. Then  $1 - g$  is a measure of the extent of the interionic attraction and permits a prediction of the behavior of strong electrolytes in moderately concentrated solutions. The Arrhenius theory for weak electrolytes takes the undissociated mole as the standard and refers the behavior of the electrolyte to it, and emphasizes the quantity  $i$  which is always greater than unity. The interionic attraction theory for strong electrolytes takes the completely ionized material as the standard and emphasizes the quantity  $g$  which is always less than unity.

In Fig. 127 the quantity  $(1 - g)$  is plotted against the total concentration of ions, i.e., against  $\nu m$  where  $\nu$  is the maximum number of ions (1, 2, 3, etc.) formed by the electrolytic dissociation of the ions and  $m$  is the number of moles per 1000 g. of solvent. In very dilute solutions where  $m$ , and hence  $\nu m$  approach zero, the interionic attraction is negligible,  $g$  approaches unity and  $1 - g$  approaches 0. Thus all curves start from the origin. As is generally evident from an examina-

tion of Table XII, the greater the number of charges on an ion, the greater is the departure of the behavior of the solution from behavior at infinite dilution as indicated by the value of  $(1 - g)$ .

The interionic attraction theory explains not only the influence of concentration on the osmotic properties of strong electrolytes, but it explains also the effect of electrolytes on the solubility of salts. The effect of a common ion in decreasing the solubility of a difficultly soluble salt was treated under the discussion of the solubility product, but this relation fails to hold accurately if the solution contains a high concentration of electrolytes. It does not apply to highly soluble salts nor does it account for the *increase* in solubility produced by the addition of other electrolytes which do not have a common ion. The solubility of thallous chloride in various salt solutions\* comprised one of the first investigations to show the influence of an excess of electrolytes on solubility. In pure water thallous chloride dissolves to the

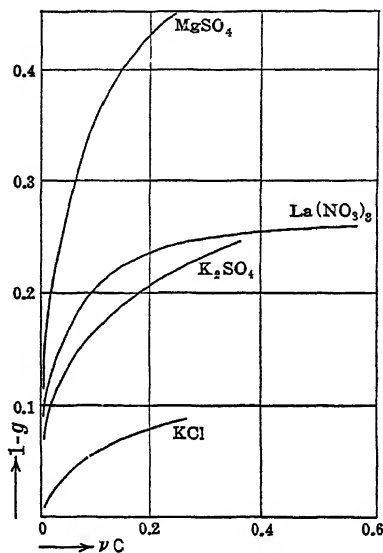


FIG. 127

extent of about 0.016 mole per liter; when potassium chloride is added, the solubility is decreased, but when potassium nitrate is added, the solubility is increased — one-tenth of a mole per liter raising the solubility to 0.019 mole per liter. Potassium nitrate contains no ion common with thallous chloride, and it might be expected to have no effect. It will be remembered that in a saturated solution there is a dynamic equilibrium with molecules or ions going into solution from the crystal and returning to the crystal. The rate of escape of ions from the crystal is not influenced by the addition of electrolytes to the solution, but the number of collisions on the crystal from solution is decreased by the addition of ionized substances because each positive ion is drawn in toward the body of the solution by a mass of negative ions and each negative ion by a mass of positive ions. A greater total concentration is required in the presence of extra ions to give an *effective* concentration sufficient to maintain equilibrium conditions with the crystal. Consequently, the analytically determined solu-

\* Bray and Winninghoff, *J. Am. Chem. Soc.*, **33**, 1663 (1911).

bility is increased. It is fair to imagine that potassium chloride itself exerts (1) an effect of interionic attraction which tends to increase the solubility of thallous chloride, and (2) a common-ion effect which tends to decrease the solubility.

The increase in solubility due to the addition of any electrolyte

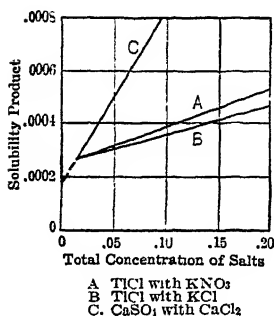


FIG. 128

leads to a corresponding increase in the solubility product as more electrolyte is added. In Fig. 128 are shown the results with the uni-univalent electrolyte, thallous chloride, and the bi-bivalent electrolyte, calcium sulfate. The deviations in the latter are much greater than in the former, as is to be expected on account of the higher ionic strength and the greater interionic attraction of the divalent calcium and sulfate ions. If equation (24) for the solubility product applied rigorously, all the lines

would be horizontal.

The decrease in effective concentration of ions at the surface of a solution, produced by the addition of other electrolytes, and the departure from the ideal behavior as the solution of strong electrolytes becomes more concentrated can now be offered as an explanation of the need for activity coefficients in understanding the electromotive force of solutions. The potential of an electrode immersed in a solution of its ions is determined in part by the frequency with which the ions collide with the surface of the electrode. When this effective concentration is decreased the potential will become less positive if the electrode exchanges electrons with positive ions in contact with it, and less negative if it exchanges electrons with negative ions. When a given potential is registered by an electrode in a very dilute solution of its ions, the potential should change by  $RT/nF \log 10$  or  $0.059/n$  volt at  $25^\circ$  for a tenfold increase in concentration. However, the change will be less than this because the interionic attraction and the correction for effective concentration at a surface will be greater in the more concentrated solution. This correction for effective concentration is determined by experiment and designated as the activity coefficient.

The interionic attraction theory in the quantitative form developed by Debye and Hückel makes it possible to calculate these activity coefficients in dilute solutions.

**The Debye-Hückel Theory.** The interionic attraction theory has already been employed to explain in a qualitative way various phe-

nomena involving ions. It was shown on page 502 that the mutual attraction between positive and negative ions at ordinary concentrations leads to a smaller decrease in vapor pressure than is to be expected on the assumption of complete separation at infinite dilution. This effect leads also to similar decreases in the freezing-point depression and other colligative properties. Abnormalities in solubilities and solubility products and single electrode potentials were interpreted also on the basis of this theory. The change in electrical conductances of strong electrolytes with concentration was also explained by the theory.

The idea of complete dissociation of strong electrolytes and the interionic attraction theory have been incorporated into the quantitative theory of Debye and Hückel.\* This theory has been remarkably successful when applied to dilute solutions.

The mathematical development of the Debye-Hückel theory is given in the appendix on page 667. It is based on the work required to separate the ions in the process of dilution. The attractive or repulsive forces are governed by Coulomb's law of charged bodies and depend on the magnitude of the ionic charges and the distance between ions as given by the expression  $e_1 e_2 / D r^2$ , where  $e_1$  and  $e_2$  represent the charges,  $D$  the dielectric constant of the solvent, and  $r$  the average distance between them. In very dilute solutions  $r$  becomes so great that this attractive force approaches zero and the simple laws of complete dissociation are adequate. Debye and Hückel derived the following expression, which holds for strong electrolytes in dilute solution:

$$-\ln \gamma_i = \frac{e^2 z_i^2}{(D k T)^{3/2}} \sqrt{\frac{2\pi N \mu}{1000}} \quad [25]$$

where  $\gamma_i$  = activity coefficient of ion species  $i$  (page 461).

$z_i$  = valence of ion species  $i$ .

$e$  = charge of an electron =  $4.803 \times 10^{-10}$  electrostatic unit.

$D$  = dielectric constant of the solution = 78.56 for water at 298° K.

$N$  = Avogadro's number =  $6.023 \times 10^{23}$ .

$k$  = gas constant per molecule =  $R/N = 1.3805 \times 10^{-18}$  erg/deg.

$\mu$  = ionic strength =  $\frac{1}{2}(c_1 z_1^2 + c_2 z_2^2 + c_3 z_3^2 + \dots)$ , the summation being taken over all the ions in the solution.

$c_i$  = concentration of ion species  $i$  in moles per liter.

\* Debye and Hückel, *Physik. Z.*, **24**, 185, 305 (1923); Noyes, *J. Am. Chem. Soc.*, **46**, 1080, 1098 (1924); **47**, 2122 (1925).



Equation (25) shows that in dilute solution the activity coefficient of an ion depends only on its valence, the ionic strength, the dielectric constant of the medium, and the temperature. Hence all univalent ions for example, (both positive and negative), in the same solution will have the same activity coefficients.

If we introduce the mean activity coefficient  $\gamma$  of the electrolyte (page 463) and put in numerical values for water at 25°, equation (25) becomes, for an electrolyte composed of just two kinds of ions,

$$-\log \gamma = 0.509 z_1 z_2 \sqrt{\mu} \quad [26]$$

The numerical constant will be different for solvents other than water and for temperatures other than 25°. In this equation  $z_1$  and  $z_2$  are the valences (without regard for the sign) of the ions of the electrolyte.

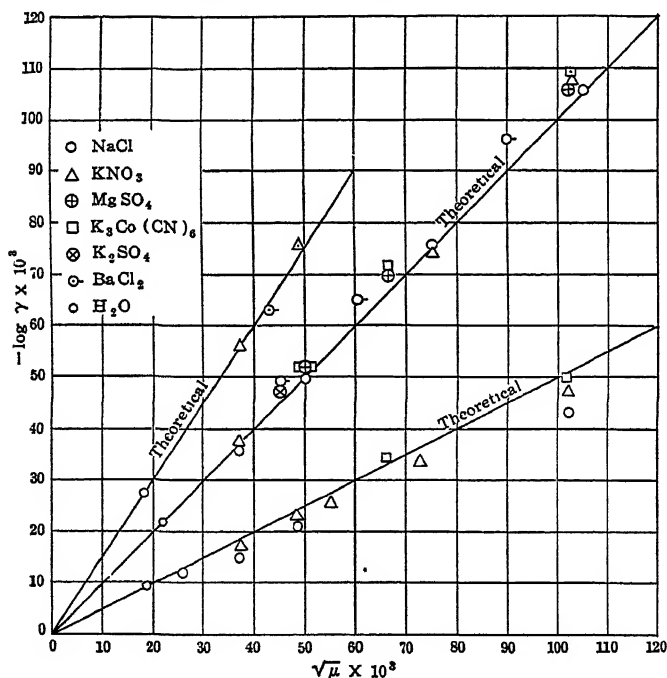


FIG. 129

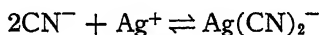
A test of this equation is shown in **Fig. 129**. Brönsted and LaMer\* determined the solubility of certain complex cobalt amines in salt solutions of various valence types and compared the solubility with the solubility in pure water, thus obtaining values of the activity

\* Brönsted and LaMer, *J. Am. Chem. Soc.*, **46**, 555 (1924).

coefficients,  $\gamma$ . In Fig. 129,  $-\log \gamma$  is plotted against  $\sqrt{\mu}$ . The lowest line corresponds to a uni-univalent cobalt compound where  $z_1 z_2$  is 1, and the slope is seen to be 0.5. The ionic strength of the solution rather than the specific nature of the added salt determines the value of  $\gamma$ . The next line corresponds to a cobalt salt of the uni-bivalent type where  $z_1 z_2$  has a value of 2, and the slope is  $2 \times 0.5 = 1$ . The steepest line in Fig. 129 corresponds to a uni-trivalent compound where  $z_1 z_2$  is 3, and the slope is 1.5. This equation gives a theoretical justification for the ionic strength  $\mu$  which Lewis found, empirically, to be of considerable importance in the study of electrolytes. It emphasizes the fact that *in dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength*.

**Concentrated Solutions.** Thus far the discussion has been concerned only with behavior of the solute and the mutual electrical attraction of its ions. In concentrated solutions and in certain solvents other factors are involved. In actual practice the properties of the *solution* are measured rather than the properties of the isolated solute, and chemical reaction with the solvent or with other ions must be considered.

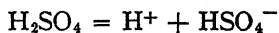
Ions sometimes combine with other ions to form *complex ions*. For example, if a solution of silver nitrate is treated with an excess of potassium cyanide, a complex ion is produced as given by the following equation:



Intermediate ions, also, may be formed as in the dissociation of sulfuric acid and other electrolytes. In very dilute solutions the reaction is



but in concentrated solutions the reaction is



There is ample evidence that many solutes combine with the water to form hydrates. The term *solvates* is more general, applying as it does to any solvent. This evidence includes color changes, shifts of absorption bands, deviations from Beer's law of light absorption, abnormal osmotic properties, abnormal conductance values, transport of solvent along with solute in electrolysis; transference numbers, etc.

The formation of ion-hydrates or ion-solvates is easily interpreted as being due to an ion-dipole attraction. The ions have a definite positive or negative charge, and the molecules of those solvents, such as water,

ammonia, and alcohol, which produce electrolytic dissociation, have large dipole moments. There is a definite force of attraction between two such units. Liquids of small dipole moment such as benzene and carbon tetrachloride fail to dissolve the alkali halides and other electrolytes which might be expected to ionize. In fact it is the reaction between solute and solvent, the ion-dipole interaction, which provides energy sufficient to separate the solid into its ions and put them into solution.

Another result of this interaction between ion and solvent is a profound change in the nature of the solvent (water, for example, in the

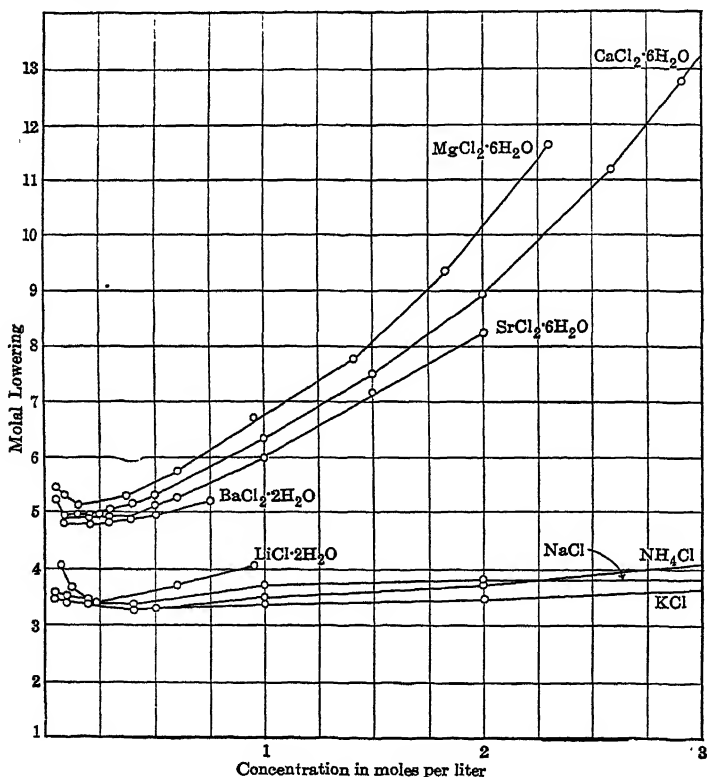


FIG. 130

concentrated solutions). The phenomenon of "salting out" is one result of this change. Nonelectrolytes such as ether are thrown out of a saturated solution, when sodium chloride is added. Also, gases like hydrogen are less soluble in salt solutions. This change in the nature of the solvent by the addition of large amounts of electrolytes is strikingly illustrated by Fig. 130. The depression of the freezing

point *per mole* of solute decreases in the more concentrated solutions as is to be expected from Fig. 69, page 225, but then the continued addition of electrolytes causes the molal depression to increase. The increase in the molal depression becomes very marked at great concentrations; in fact, in a molal solution it is frequently greater than the molal depression multiplied by the number of ions produced. This phenomenon, which is quite general, may be explained by assuming that the dissolved substance has entered into combination with a portion of the water, thus removing it from the role of solvent.

Those solutes which exhibit the greatest abnormal action on the freezing point of water should be the ones which crystallize from the solution with the greatest amount of water of crystallization. That there is a relation between freezing-point depression and water of crystallization is shown by the curves in Fig. 130. In concentrated solutions those salts of a given number of ions which crystallize without water of crystallization produce the least depression of the freezing point. Those crystallizing with two molecules of water produce more, and those with six molecules still more. Similar relations are found to hold for the corresponding bromides, iodides, and nitrates.

**Summary of Concentration Ranges.** It may be concluded from what has been said in this chapter that aqueous solutions of electrolytes may be classified roughly into four different groups depending on the concentration.

In exceedingly dilute solutions (less than  $0.0001\ M$  for strong electrolytes and much less for weak electrolytes) the solute is completely dissociated, in agreement with either the Arrhenius or the interionic attraction theory.

In dilute solutions ( $0.0001$  to  $0.01\ M$ ) the Arrhenius theory is satisfactory only for weak electrolytes such as acetic acid, and the theory of interionic attraction is necessary and adequate for strong electrolytes.

In solutions of moderate concentration ( $0.01\ M$  to  $1\ M$ ) the properties of strong electrolytes are affected both by interionic attraction and by the presence of un-ionized molecules. The mere fact that one can smell hydrochloric acid molecules from a  $1\ M$  solution of  $\text{HCl}$  proves that some undissociated molecules exist in the solution. Exact theoretical calculations cannot yet be made in this region.

In concentrated solutions (greater than  $1\ M$ ) the character of the solvent is markedly changed by the presence of the solute and the situation is very complicated. Hydration or solvation of the solute and depolymerization of the solvent may be factors.

These classifications are to be taken only as rough approximations,

and they vary greatly for different electrolytes. Apparently some salts, such as mercuric chloride and cadmium chloride, are only very slightly dissociated even in dilute solution.

In nonaqueous solutions with low dielectric constants the interpretation is more difficult and, in general, the solutions must be more dilute than the aqueous solutions before the theoretical equations can be applied.

**Theories of Conductance.\*** Although theories of conductance do not properly belong in a chapter on ionic equilibria the following brief discussion has been postponed until after the presentation of the interionic attraction theory. The earlier attempts to explain the phenomena of the electrical conductance of strong electrolytes were handicapped by an overemphasis of the Arrhenius theory and a lack of data concerning nonaqueous solutions. Rapid advances following the Debye-Hückel theory of interionic attraction, broader investigations with different solvents, including those of low dielectric constant and improved experimental techniques, now permit a fairly quantitative understanding of the conductance behavior of dilute aqueous solutions and extremely dilute non-aqueous solutions. Moreover the causes of deviations in the more concentrated solutions are now known at least in part. The aqueous solutions and the solutions of high dielectric constant are still the simplest to interpret. It will be remembered that the conductance depends on both the number of ions and the velocity of the ions. In strong electrolytes the ionization is so complete that the changes in equivalent conductance are concerned with the velocity of the ions.

According to the present theory each ion in a solution is surrounded by an ionic atmosphere of central symmetry, resulting from the combined effect of Coulomb forces between the charged ions and the thermal agitation. When an external potential is applied, the electrical force overcomes the ordinary frictional resistance to the motion of the ions and they move toward the electrode of opposite charge. This motion, however, sets up two retarding forces. The first, known as the relaxation force, is the result of the movement of the ion from

\* Additional material on this subject may be found in the following references.

Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Co., New York, 1942, pp. 148-169; Kraus, "The Present State of the Problem of Electrolytic Solutions," *J. Chem. Education*, **12**, 567 (1935); MacInnes, "The Interionic Attraction Theory of Electrolytes," *Science*, **86**, 23 (1937); "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939, Chapters 18 and 19; Fuoss, "Properties of Electrolytic Solutions," *Chem. Rev.*, **17**, 27 (1935); Davidson, "Recent Advances in the Electrochemistry of Non-Aqueous Solutions," *J. Chem. Education*, **14**, 218 (1937).

the center of its atmosphere under the influence of the applied potential. Since the atmosphere requires a finite time for its formation, a portion of the atmosphere will lag behind its normal position producing a dissymmetry in the direction of motion and causing the ion to suffer a reduced mobility.

The second retarding force arises from an electroosmotic motion of the solvent in the direction opposite to that of the ion in question. The effect of each of these forces can be expressed in ordinary conductance units as pointed out by Debye and Hückel, and Onsager,\* thus

$$\Lambda = \Lambda_0 - \Lambda_I - \Lambda_{II} = \Lambda_0 - a\sqrt{c}\Lambda_0 - b\sqrt{c} \quad [27]$$

where  $\Lambda_0$  is the conductance at infinite dilution,  $\Lambda_I$  is the relaxation force and  $\Lambda_{II}$  is the electrophoretic force,  $c$  is the concentration and  $a$  and  $b$  are theoretical constants derived from a mathematical treatment of this ionic atmosphere. For a uni-univalent strong electrolyte in water at 25°, equation (27) is

$$\Lambda = \Lambda_0 - (59.8 + 0.227\Lambda_0)\sqrt{c} \quad [28]$$

In an alternating field each ion in solution will acquire a periodic reaction. If the frequency is increased to a point where the period of oscillation of the ion becomes comparable with the time of relaxation the dissymmetry in the ionic atmosphere will decrease, the effect of the electrical force of relaxation will diminish and the equivalent conductance will increase. Also by the application of very high voltages the ion may be forced to move fast enough to escape completely from its atmosphere, so that both retarding forces disappear and the equivalent conductance approaches its limiting value at infinite dilution. Debye, Falkenhagen, Wien, and Onsager have all made theoretical studies of frequency and field strength and the results are in general accord with the experimental facts.

Fuoss has developed an equation which gives straight lines when the function  $\Lambda_0/\Lambda$  (corrected for interionic attraction) is plotted against a function of the concentration and the square of the activity coefficient. It applies in dilute solutions to all electrolytes in various solvents. In solvents of low dielectric constant (below 10) it applies only to the extremely dilute solutions and a minimum is observed in the curve at higher concentrations. This behavior is due to the formation of a complex between a molecule and one of the ions. Such combinations do not occur in solutions of high dielectric constant.

In benzene and other solvents of extremely low dielectric constant there is a combination of ions and molecules into still larger aggregates

\* Onsager, *Physik. Z.*, **28**, 277 (1927).

as shown, for example, in the abnormally small depression of the freezing point. The abnormalities are greatest in the case of small ions with large dipole moments.

In general, the properties of an electrolytic solution depend on the solvating power and the dielectric constant of the solvent, and on the size, configuration, and space distribution of the ions. In water which has a dielectric constant of 78 and a marked tendency to combine with ions there is no detectable difference in the ionization of potassium chloride, potassium bromide, and potassium iodide, but there is a marked difference in liquid ammonia which has a dielectric constant of 22 and a lesser tendency to solvate. At  $-34^\circ$  in ammonia, the dissociation constants for potassium iodide and chloride are respectively 0.0042 and 0.00087. Those electrolytes with the largest ions are the most highly dissociated in a given solvent.

The generalizations discussed in this section apply only to dilute solutions. In concentrated solutions the phenomena are too complicated to describe with mathematical formulas yet devised. Finally, it should be pointed out that electrical conduction is an irreversible process and that it is distinct from freezing-point lowering and other reversible processes which are of interest in thermodynamics.

#### REFERENCES

- GLASSTONE, "Introduction to Electrochemistry," D. Van Nostrand Co., New York, 1942.  
 MACINNES, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, 1939.  
 HAMMETT, "Solutions of Electrolytes," McGraw-Hill Book Co., New York, 1936.  
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#### PROBLEMS

1. The specific conductance at  $25^\circ$  of propionic acid ( $\text{CH}_3\text{CH}_2\text{COOH}$ ) in 0.0156 *N* solution is 0.0001752 reciprocal ohms, and  $\Lambda_0 = 386$ . Calculate (a) the degree of dissociation into ions, (b) the concentration of hydrogen ions in the solution, and (c) the ionization constant of propionic acid at  $25^\circ$ .

*Ans.* (a) 0.0291. (b)  $4.53 \times 10^{-4}$  gram-ions per liter. (c)  $1.35 \times 10^{-5}$ .

2. The dissociation constant for formic acid,  $\text{HCOOH}$ , is  $2.14 \times 10^{-4}$  at  $25^\circ$ . What is the hydrogen-ion concentration of a 0.1 *M* solution at  $25^\circ$  assuming activities equal to concentrations?

*Ans.* 0.00452 gram-ions per liter.

3. At  $40^\circ$  the ionization constant of ammonium hydroxide is  $2 \times 10^{-6}$ . (a) What is the  $\text{OH}^-$  ion concentration in a 0.1 *m* solution? (b) What is the  $\text{OH}^-$  ion concen-

tration of a solution 0.1 *m* with respect to ammonium hydroxide which is also 0.1 *m* with respect to ammonium chloride, assuming the latter to be completely ionized?

*Ans.* (a)  $1.4 \times 10^{-3}$ . (b)  $2.0 \times 10^{-5}$ .

4. The ionization constant of ammonium hydroxide is  $1.4 \times 10^{-5}$  at 0° and  $2 \times 10^{-5}$  at 40°. What is the average heat of ionization of ammonium hydroxide in this range of temperature?

*Ans.* +1516 cal.

5. The electromotive force of the cell

Pt, (H<sub>2</sub> (1 atm.); C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>·HCl (0.03125 *m*)) || normal calomel electrode

is 0.464 volt at 25°. Calculate the per cent hydrolysis of the aniline hydrochloride.

*Ans.* 2.5 per cent.

6. The hydrolysis constant of aniline hydrochloride is  $2.25 \times 10^{-5}$ , and the ionization constant of aniline is  $4.2 \times 10^{-10}$  at 25°. Calculate the concentration of the H<sup>+</sup> and OH<sup>-</sup> ions in water.

*Ans.*  $c_{H^+} = c_{OH^-} = 0.97 \times 10^{-7}$ .

7. It can be shown that for an aqueous solution of a salt of a weak base and strong acid the hydrogen-ion concentration is given by:

$$C_{H^+} = \sqrt{\frac{K_w}{K_b} c_s}$$

where  $c_s$  = concentration in mole per liter.

$K_w$  = ionization constant of water.

$K_b$  = ionization constant of base.

Pyridinium perchlorate is such a salt. If  $K_b = 1.6 \times 10^{-9}$ , what is the pH of a 0.0001 molar solution?

*Ans.* 4.60.

8. The specific conductance at 25° of a saturated solution of barium sulfate was  $4.58 \times 10^{-6}$  reciprocal ohm, and that of the water used was  $1.52 \times 10^{-6}$ . The equivalent conductance at infinite dilution of barium sulfate is 143. What is the solubility of BaSO<sub>4</sub> at 25° in (a) gram-equivalents per liter, (b) moles per liter, and (c) grams per liter?

*Ans.* (a)  $2.14 \times 10^{-5}$  equivalents per liter. (b)  $1.07 \times 10^{-5}$  mole per liter.

(c)  $2.49 \times 10^{-3}$  g. per liter.

9. It is customary to express  $-\log K$  as *pK*. For the dissociation of 5-ethyl 5-hexyl barbituric acid at 25° in aqueous solution *pK* is 7.79. What is the standard free energy change ( $\Delta F^\circ$ ) for the reaction  $HA(aq.) = H^+ + A^-$ ?

*Ans.* 10,630 cal. per mole.

10. The solubility product of silver bromide at 18° is  $4.1 \times 10^{-13}$ . Calculate:

(a) The solubility of silver bromide in pure water.

(b) The solubility of silver bromide in 0.1 molar NaBr.

*Ans.* (a)  $6.40 \times 10^{-7}$  moles per liter. (b)  $4.1 \times 10^{-12}$  moles per liter.

11. At 25° the potential of the cell

Ag, AgI; KI (1 *m*) || AgNO<sub>3</sub> (0.001 *m*); Ag

is -0.72 volt. In a molal solution of KI the activity coefficient of I<sup>-</sup> ion is 0.65 and in 0.001 *m* AgNO<sub>3</sub> the activity coefficient of Ag<sup>+</sup> ion is 0.98. (a) What is the solubility product of AgI? (b) Assuming no salt effect, what would be the solubility of AgI in pure water?

*Ans.* (a)  $4.2 \times 10^{-16}$ . (b)  $2.1 \times 10^{-8}$  mole per 1000 g. H<sub>2</sub>O.



12. What is the ionic strength of 0.5 *M* solutions of (a)  $\text{CaCl}_2$ , (b)  $\text{Al}_2(\text{SO}_4)_3$ , (c)  $\text{K}_3\text{PO}_4$ , (d)  $\text{NaHCO}_3$ .

Ans. (a) 1.5. (b) 7.5. (c) 3. (d) 1.5.

13. From the following tables of freezing points calculate *g* and plot  $1 - g$  against

NaCl		$\text{K}_4\text{Fe}(\text{CN})_6$	
<i>c</i>	$\Delta T_f/m$	<i>c</i>	$\Delta T_f/m$
0.01	3.604	0.0075	6.9
0.04	3.53	0.025	6.17
0.2	3.424	0.075	5.41
0.7	3.36	0.191	4.80

14. At 25° the equivalent conductance of propionic acid at infinite dilution is 385.6 ohms and the ionization constant is  $1.34 \times 10^{-5}$ . Calculate the equivalent conductance of a 0.05 *N* solution of propionic acid at 25°.

15. Two grams of lactic acid is diluted with water to 1 liter. How many gram-ions of hydrogen are present in the solution? The dissociation constant of lactic acid is  $1.36 \times 10^{-4}$  at 25°.

16. At 25° the ionization constant of  $\alpha$ -bromopropionic acid is  $1.06 \times 10^{-3}$  and that for  $\beta$ -bromopropionic acid is  $9.5 \times 10^{-5}$ . What are the relative strengths of these two acids?

17. Calculate the *pH* at 25° of a buffer solution containing 50 ml. of 0.2 *M* potassium hydrogen phthalate and 45.45 ml. of 0.2 *M* NaOH solution all diluted to 200 ml. The dissociation constant for the second hydrogen of phthalic acid at 25° is  $3.1 \times 10^{-5}$ .

18. Alanine is an amino acid which dissociates into both  $\text{H}^+$  and  $\text{OH}^-$  ions. At 25° the dissociation constant for the dissociation into anions and hydrogen ions is  $1.99 \times 10^{-10}$ . The apparent dissociation constant for the dissociation into cations and hydroxyl ions is  $5.25 \times 10^{-12}$ . At what *pH* would you expect the osmotic pressure of an alanine solution to be a minimum?

19. (a) What is the hydrogen-ion concentration of a 2 molar solution of  $\text{NH}_4\text{Br}$  at 25° after hydrolysis? The ionization constant of  $\text{NH}_4\text{OH}$  is  $1.8 \times 10^{-5}$ . (b) What is the *pH*?

20. The specific conductance of a saturated solution of thallous bromide at 20° is  $2.158 \times 10^{-4}$  and the specific conductance of water at the same temperature is  $0.044 \times 10^{-6}$  reciprocal ohms. The equivalent conductance at infinite dilution is 138.3. Calculate the solubility of thallous bromide in grams per liter.

21. The solubility of strontium oxalate at 20° is 0.00054 mole per liter. What is the solubility product? How much strontium oxalate would dissolve in a solution having an oxalate-ion concentration of 0.04 gram-ion per liter?

22. From the following tables of freezing points, calculate *g*, and plot  $1 - g$  against  $\nu m$ , where  $\nu$  is the number of ions produced from one molecule and *m* is the molality.

KCl		$\text{K}_3\text{Fe}(\text{CN})_6$	
<i>m</i>	$\Delta T_f/m$	<i>m</i>	$\Delta T_f/m$
0.02	3.566	0.002	6.87
0.05	3.503	0.005	6.53
0.10	3.451	0.01	6.26
0.20	3.394	0.02	5.98
		0.05	5.60

23. What is the ionic strength of 0.02 *m* solutions of each of the following substances: (a) LiCl, (b) K<sub>2</sub>SO<sub>4</sub>, (c) MgSO<sub>4</sub>, (d) Na<sub>3</sub>PO<sub>4</sub>, (e) K<sub>4</sub>Fe(CN)<sub>6</sub>?

24. To show that  $\Delta/\Delta_0$  and  $i/\nu$  or  $g$  are not equal for strong electrolytes the following data are helpful. The expression  $i/\nu$  or  $g$  is determined under static or equilibrium conditions; the expression  $\Delta/\Delta_0$  under dynamic conditions. Determine values of the two for 0.1 *m* MgSO<sub>4</sub> from the following data:

Freezing point of 0.1 *m* MgSO<sub>4</sub> = -0.225°.

$\Delta$  for 0.1 *m* MgSO<sub>4</sub> at 0° = 26.5.

$\Delta_0$  for MgSO<sub>4</sub> at 0° = 64.

It will be noted that the agreement is not within the limits of experimental error, indicating that there is a fundamental difference between the two methods, and that  $\Delta/\Delta_0$  cannot be interpreted simply as a "degree of dissociation."

25. The equivalent conductance of 0.01 *N* acetic acid at 25° is 16.3 reciprocal ohms. At infinite dilution it is 390.7. (a) Calculate the degree of dissociation of acetic acid at this concentration. (b) Calculate the vapor-pressure lowering produced by 1 g. of acetic acid in a liter of water, assuming that 1 liter of this dilute solution contains 1000 g. of water.

26. How many hydrogen ions are there in 100 ml. of an 0.1 molar solution of an acid which has a dissociation constant of (a)  $1 \times 10^{-3}$ ; (b)  $1 \times 10^{-10}$ ; (c)  $6 \times 10^{-23}$ ?

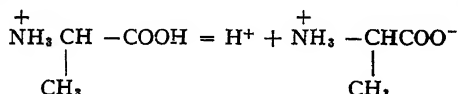
27. For benzoic acid at 25° the ionization constant is  $7.3 \times 10^{-5}$ . Calculate the pH of a 0.0001 molar solution of benzoic acid at 25°.

28. Derive a general equation for calculating the degree of dissociation for an electrolyte which dissociates into three ions, as for example, oxalic acid ( $(\text{COOH})_2 = 2\text{H}^+ + \text{C}_2\text{O}_4^{2-}$ ). Give the approximate formula assuming that  $\alpha$  is very small.

29. The ionization constants at 25° for acetic acid, lactic acid, and bromoacetic acid are  $1.8 \times 10^{-5}$ ,  $1.4 \times 10^{-4}$ , and  $1.4 \times 10^{-3}$  respectively. (a) Calculate  $\alpha$  for a 0.01 molar solution of each of these acids by the approximate method (assuming  $1 - \alpha = 1$ ) and (b) by the exact method.

30. Leucylglycine is an amino acid which dissociates into both  $\text{H}^+$  and  $\text{OH}^-$  ions. At 25° the dissociation constant for the dissociation into anions and hydrogen ions is  $1.51 \times 10^{-8}$ . The apparent dissociation constant for the dissociation into cations and hydroxyl ions is  $3.02 \times 10^{-11}$ . Calculate the pH at which the degree of dissociation into hydrogen ions and hydroxyl ions is the same.

31. Alanine dissociates in the following manner in acid solutions:

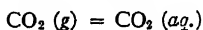


and

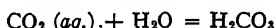
$$K = \frac{c_{\text{H}^+} \times c_{\text{R}^+}}{c_{\text{R}^+}} = 0.0040$$

In a solution whose pH is 3, what is the per cent dissociation of the alanine?

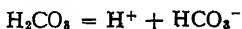
32. Gas containing 20% O<sub>2</sub>, 78% N<sub>2</sub>, 0.3% CO<sub>2</sub>, and the rest noble gases is confined above distilled water at room temperature. What is the pH of the water? What is the concentration of the H ions?



$$K_p = 0.0333 \text{ (atm.)}$$



$$K_s = \frac{c_{\text{H}_2\text{CO}_3}}{c_{\text{CO}_2}} = 6.8 \times 10^{-3}$$



$$K_i = 3 \times 10^{-7}$$

33. The specific conductance of a saturated solution of AgCl in water was found to be  $2.279 \times 10^{-6}$  mhos. The specific conductance of the water used was  $1.16 \times 10^{-6}$  mhos. Using the table of ionic conductances calculate:

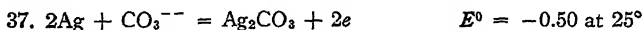
(a) The solubility of AgCl in grams per liter.

(b) The solubility product of AgCl.

34. A solution of sodium chloride has an ionic strength of 0.24. (a) What is its concentration? (b) What concentration of  $\text{Na}_2\text{SO}_4$  would have the same ionic strength? (c) What concentration of  $\text{MgSO}_4$ ?

35. What is the ionic strength of a 0.4 *m* solution of: (a)  $\text{MnCl}_2$ ; (b)  $\text{MnSO}_4$ ; (c)  $\text{AuCl}_3$ ; (d)  $\text{Fe}_2(\text{SO}_4)_3$ ?

36. A solution of 9.94 g. of  $\text{Na}_2\text{SO}_4$  in 1000 g. of water produces the same lowering of the vapor pressure as an 0.169 molal solution of urea. What is the osmotic coefficient *g* in this solution. Urea does not dissociate.

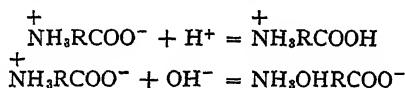


What is the solubility of  $\text{Ag}_2\text{CO}_3$  in moles per liter at this temperature?

38. The first ionization constant of  $\text{H}_2\text{S}$  in water is  $9.1 \times 10^{-8}$ ; the second is  $1.2 \times 10^{-15}$ . The solubility of  $\text{H}_2\text{S}$  in water is 3.4 g. per liter. How many grams of Pb ( $\text{NO}_3$ )<sub>2</sub> added to 1 liter of saturated  $\text{H}_2\text{S}$  solution will just start precipitation of PbS?

39. Show that if  $K_a$  and  $K_b$  do not differ by more than a hundred-fold the  $\text{H}^+$  concentration and the  $\text{OH}^-$  concentration will be *practically* equal.

40. Proteins probably exist in solution as dipole-ions or ("zwitterions"), i.e., an ion having both a negative and a positive charge. The effect of the addition of acids or bases to such substances may be seen from the equations:



Show that the actual ionization constant as an acid is equal to the hydrolysis constant of the basic part, and vice versa.

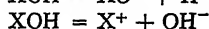
41. Calculate the free energy of neutralization of a mole of strong acid by a mole of strong base in a dilute aqueous solution at  $25^\circ$ ,  $K_w$  being  $10^{-14}$ .

42. In the case of the hydrolysis of a salt of a strong base and weak acid show that

$$c_{\text{H}^+} = \sqrt{\frac{K_a K_w}{c}}$$

where  $K_a$  = ionization constant of the acid,  $K_w$  = ionization constant of water, and  $c$  = concentration of salt in moles per liter. Derive the expression for the pH of such a solution. How will an increase in concentration of salt affect the pH of the solution? Test this by determining the pH of 0.1 *N* and of 1 *N* sodium isobutyrate at  $25^\circ$  ( $K_a = 0.98 \times 10^{-5}$ ).

43. Given an amphoteric electrolyte XOH capable of dissociating according to both of the equations



If the basic dissociation constant is  $K_b$  and the acidic dissociation constant  $K_a$ , derive the expression for the hydrogen-ion concentration in a solution of this electrolyte as a function of the concentration of the un-ionized substance.

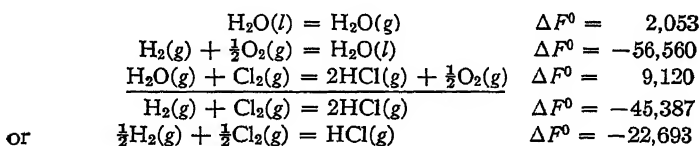
## CHAPTER XVIII

### CHEMICAL THERMODYNAMICS

**Calculation of Free Energy.** The important relations between equilibrium constants, free energy changes, and electromotive force of galvanic cells have been discussed in earlier chapters. In this chapter the further application of thermodynamical principles to chemical calculations will be described briefly, using the notation of Lewis and Randall as described in their "Thermodynamics and the Free Energy of Chemical Substances."

If the free energy change in a chemical reaction cannot be determined directly from equilibrium measurements or from electrode potentials, it can often be calculated indirectly from other reactions for which the free energy changes are known. If several reactions are added together, the free energy changes are additive just as heats of reaction are additive. The free energy change of the total reaction is the sum of the free energy changes of all the composite reactions. Free energies are usually given in calories.

*Example 1.* Calculate the free energy of formation of hydrochloric acid from its elements at 25° from the following data



Just as there are tables of heats of formation (page 115) from which heats of reaction can be calculated, so also are there tables of free energy of formation from which  $\Delta F^0$  for various reactions can be calculated. The free energies of the elements at 25° and atmospheric pressure, in their most stable states under these conditions, are taken as zero. The free energy of formation  $\Delta F^0$  of a compound is the change in free energy involved when one mole of this substance in its standard state at 25° and 1 atm. pressure is produced from the elements in their standard states (25° and 1 atm. pressure). If the substance is not in its standard state the superscript zero is omitted. A table giving a few of these values follows.

TABLE I

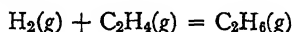
FREE ENERGIES OF FORMATION AT 25° AND 1 ATMOSPHERE\*

Substance	$\Delta F_{298 \text{ K}}^0$	Substance	$\Delta F_{298 \text{ K}}^0$
Water, $\text{H}_2\text{O}(l)$	-56,560	Propylene, $\text{C}_3\text{H}_6(g)$	14,730
Water, $\text{H}_2\text{O}(g)$	-54,507	Acetylene, $\text{C}_2\text{H}_2(g)$	50,034
Hydrochloric acid, $\text{HCl}(g)$	-22,692	<i>cis</i> -2-Butene, $\text{C}_4\text{H}_8(g)$	15,570
Hydrobromic acid, $\text{HBr}(g)$	-12,540	<i>trans</i> -2-Butene, $\text{C}_4\text{H}_8(g)$	14,800
Hydroiodic acid, $\text{HI}(g)$	315	Formaldehyde, $\text{CH}_2\text{O}(g)$	-26,100
Sulfur, S(rhombic)	0	Formic acid, $\text{CH}_2\text{O}_2(g)$	-82,520
Sulfur, S(monoclinic)	18	Formic acid, $\text{CH}_2\text{O}_2(l)$	-85,150
Sulfur, S(g)	30,240	Methanol, $\text{CH}_4\text{O}(l)$	-39,960
Hydrogen sulfide, $\text{H}_2\text{S}(g)$	-7,840	Urea, $\text{CH}_4\text{N}_2\text{O}(s)$	-47,120
Ammonia, $\text{NH}_3(g)$	-3,910	Oxalic acid, $\text{C}_2\text{H}_2\text{O}_4(s)$	-165,900
Nitric oxide, $\text{NO}(g)$	20,850	Acetic acid, $\text{C}_2\text{H}_4\text{O}_2(l)$	-94,500
Nitrogen dioxide, $\text{NO}_2(g)$	11,920	Ethyl bromide, $\text{C}_2\text{H}_5\text{Br}(l)$	-6,180
Carbon monoxide, $\text{CO}(g)$	-32,700	Ethanol, $\text{C}_2\text{H}_6\text{O}(l)$	-40,200
Carbon dioxide, $\text{CO}_2(g)$	-94,100	Dimethyl ether, $\text{C}_2\text{H}_6\text{O}(g)$	-26,350
Lead oxide, $\text{PbO}(s)$	-45,050	Ethylene glycol, $\text{C}_2\text{H}_6\text{O}_2(l)$	-80,200
Silver ion, $\text{Ag}^{++}$	18,448	Acetone, $\text{C}_3\text{H}_6\text{O}(g)$	-36,500
Zinc ion, $\text{Zn}^{++}$	-34,984	Acetone, $\text{C}_3\text{H}_6\text{O}(l)$	-37,220
Methane, $\text{CH}_4(g)$	-12,085	Glycerol, $\text{C}_3\text{H}_8\text{O}_3(l)$	-113,600
Ethane, $\text{C}_2\text{H}_6(g)$	-7,787	Fumaric acid, $\text{C}_4\text{H}_4\text{O}_4(s)$	-156,700
Propane, $\text{C}_3\text{H}_8(g)$	-5,550	Maleic acid, $\text{C}_4\text{H}_4\text{O}_4(s)$	-149,400
<i>n</i> -Butane, $\text{C}_4\text{H}_{10}(g)$	-3,630	Ethyl acetate, $\text{C}_4\text{H}_8\text{O}_2(l)$	-77,600
<i>iso</i> -Butane, $\text{C}_4\text{H}_{10}(g)$	-4,160	Diethyl ether, $\text{C}_4\text{H}_{10}\text{O}(l)$	-28,300
<i>n</i> -Pentane, $\text{C}_5\text{H}_{12}(g)$	-1,620	Benzene, $\text{C}_6\text{H}_6(g)$	30,640
2-Methyl butane, $\text{C}_5\text{H}_{12}(g)$	-3,190	Benzene, $\text{C}_6\text{H}_6(l)$	29,400
Tetramethyl methane, $\text{C}_5\text{H}_{12}(g)$	-3,310	Cyclohexane, $\text{C}_6\text{H}_{12}(l)$	6,800
<i>n</i> -Hexane, $\text{C}_6\text{H}_{14}(g)$	80	Cyclohexane, $\text{C}_6\text{H}_{12}(l)$	18,200
<i>n</i> -Heptane, $\text{C}_7\text{H}_{16}(g)$	1,750	Benzoic acid, $\text{C}_7\text{H}_6\text{O}_2(s)$	-60,100
<i>n</i> -Octane, $\text{C}_8\text{H}_{18}(g)$	3,400	Naphthalene, $\text{C}_{10}\text{H}_8(s)$	45,200
Ethylene, $\text{C}_2\text{H}_4(g)$	16,279	Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)$	-371,600

\* The data are taken from different sources including, Pitzer, *Chem. Rev.*, **27**, 39 (1940), and Parks and Huffman, "Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932.

† Standard state = 1 gram-equivalent per liter.

*Example 2.* The use of this table in calculating free energy changes may be illustrated with the reaction



$$\begin{aligned}\Delta F^0 &= \Delta F_{\text{products}}^0 - \Delta F_{\text{reactants}}^0 = -7,787 - (0 + 16,279) \\ &= -24,066 \text{ cal. (at } 25^\circ \text{ and } 1 \text{ atm.)}\end{aligned}$$

The calculation of free energies from equilibrium constants, and of equilibrium constants from free energies, is made by means of the

relation derived in Chapter XII.

$$\Delta F^0 = -RT \ln K \quad [1]$$

The values of the equilibrium constant and of the standard free energy change  $\Delta F^0$  in this equation both depend on the standard states used for the substances involved in the reaction. For a perfect gas the standard state is at 1 atm. pressure, and for a reaction between perfect gases the equilibrium constant calculated from equation (1) is  $K_p$ .

*Example 3.* Calculate  $K_p$  at 25° for the reaction between hydrogen and ethylene just given

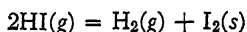
$$\Delta F^0 = -24,066 = -1.987 \times 298.1 \times 2.303 \log K_p$$

$$K_p = \frac{p_{C_2H_4}}{p_{H_2} \times p_{C_2H_6}} = \text{antilog} \frac{24,066}{1.987 \times 298.1 \times 2.303} = 5.65 \times 10^{17}$$

For a substance in dilute solution the usual standard state refers to an activity  $a$  of unity, i.e., an *effective* concentration of one mole per 1000 g. of solvent; and  $K$ , as given by equation (1), refers to  $K_c$ .

If a pure liquid or solid is present, it does not appear in the equilibrium constant.

*Example 4.* Calculate from Table I the equilibrium constant for the following reaction at 25°.



$$\Delta F^0 = 0 - 2 \times 315 = -630 \text{ cal.}$$

$$= -1.987 \times 298.1 \times 2.303 \log K$$

$$K = \frac{p_{H_2}}{p_{HI}^2} = \text{antilog} \frac{630}{1.987 \times 298.1 \times 2.303} = 2.90$$

**Influence of Temperature on Free Energy Change.** It is often necessary to calculate the free energy change of a chemical reaction at one temperature from data obtained at another temperature. Such a calculation may be made when the heat of reaction is known. Differentiating  $\Delta F/T$  with respect to temperature at constant pressure

$$\frac{\partial \left( \frac{\Delta F}{T} \right)}{\partial T} = \frac{T \frac{\partial (\Delta F)}{\partial T} - \Delta F \frac{\partial T}{\partial T}}{T^2} \quad [2]$$

But according to the Gibbs-Helmholtz equation derived on page 143, at constant pressure

$$\frac{\partial (\Delta F)}{\partial T} = \frac{\Delta F}{T} - \frac{\Delta H}{T} \quad [3]$$

Substituting into equation (2)

$$\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T} = \frac{T\left(\frac{\Delta F}{T} - \frac{\Delta H}{T}\right) - \Delta F}{T^2} = -\frac{\Delta H}{T^2} \quad [4]$$

But  $\Delta H$  depends on the temperature and on the difference between the heat capacity of the products and the reactants (page 124), as shown in the equation

$$\Delta H = \Delta H_0 + \int \Delta C_p dT \quad [5]$$

where  $\Delta H_0$  is an integration constant, a hypothetical heat of reaction at absolute zero assuming that the heat capacity relations, determined at ordinary temperatures, hold down to absolute zero. The heat capacity of a substance can usually be expressed by an empirical equation of the type

$$C_p = \Gamma_0 + \Gamma_1 T + \Gamma_2 T^2 + \dots \quad [6]$$

where  $\Gamma$  represents an empirical constant, and since the difference between the heat capacity of the reactants and the products is  $\Delta C_p$

$$\Delta C_p = C_{p \text{ (products)}} - C_{p \text{ (reactants)}} = \Delta \Gamma_0 + \Delta \Gamma_1 T + \Delta \Gamma_2 T^2 + \dots \quad [7]$$

On substituting into equation (5) and integrating

$$\begin{aligned} \Delta H &= \Delta H_0 + \int \Delta C_p dT = \Delta H_0 + \Delta \Gamma_0 T + \frac{1}{2} \Delta \Gamma_1 T^2 \\ &\quad + \frac{1}{3} \Delta \Gamma_2 T^3 + \dots \end{aligned} \quad [8]$$

and again substituting equation (8) into equation (4)

$$\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T} = \frac{-\Delta H}{T^2} = \frac{-\Delta H_0 - \Delta \Gamma_0 T - \frac{1}{2} \Delta \Gamma_1 T^2 - \frac{1}{3} \Delta \Gamma_2 T^3 - \dots}{T^2} \quad [9]$$

On integrating

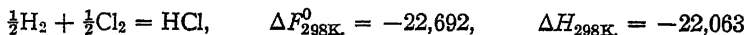
$$\frac{\Delta F}{T} = \frac{\Delta H_0}{T} - \Delta \Gamma_0 \ln T - \frac{1}{2} \Delta \Gamma_1 T - \frac{1}{6} \Delta \Gamma_2 T^2 \dots + I \quad [10]$$

and

$$\Delta F = \Delta H_0 - \Delta \Gamma_0 T \ln T - \frac{1}{2} \Delta \Gamma_1 T^2 - \frac{1}{6} \Delta \Gamma_2 T^3 \dots + IT \quad [11]$$

The integration constant  $\Delta H_0$  may be evaluated by the experimental determination of  $\Delta H$  at some temperature; and the integration constant  $I$  may be evaluated by the experimental determination of  $\Delta F$  at a definite temperature.

*Example 5.* Calculate the free energy of formation of hydrochloric acid at 1327° or 1600° K. from the free energy and heat of reaction at 25°.



By equation (5)

$$\Delta H_0 = \Delta H - \int_0^T \Delta C_p dT$$

According to the empirical equations for the heat capacities of gases (page 122)

$$\Delta C_p = C_{p,\text{HCl}} - (\frac{1}{2}C_{p,\text{H}_2} + \frac{1}{2}C_{p,\text{Cl}_2}) = 6.70 + 0.00084T$$

$$-\left(\frac{6.62 + 0.00081T}{2} + \frac{8.28 + 0.00056T}{2}\right) = -0.75 + 0.000155T$$

$$\begin{aligned} \Delta H_0 &= -22,063 + 0.75 \times 298 - \frac{1}{2} \times 0.000155 \times 298^2 = -22,063 \\ &\quad + 224 - 7 = -21,846 \end{aligned}$$

Substituting in equation (11)

$$\begin{aligned} -22,692 &= -21,846 + 0.75 \times 298 \times 2.303 \times 2.474 - \frac{1}{2} \times 0.000155 \\ &\quad \times 298^2 + 298I \end{aligned}$$

$$I = \frac{-22,692 + 21,846 - 1273 + 7}{298} = -7.087$$

and

$$\Delta F^0 = -21,846 + 0.75T \ln T - 7.75 \times 10^{-5}T^2 - 7.087T$$

This general equation may now be used to calculate the free energy of formation of hydrochloric acid at any temperature for which the heat capacity equations are valid.

$$\begin{aligned} \Delta F_{1600\text{K}}^0 &= -21,846 + 0.75 \times 1600 \times 2.303 \times 3.204 - 7.75 \times 10^{-5} \\ &\quad \times 1600^2 - 7.087 \times 1600 = -24,528 \end{aligned}$$

Hydrochloric acid is less stable at the higher temperature. This difference in stability is easily seen by comparing the equilibrium constants.

At 25°,  $\Delta F^0 = -22,692$  and  $K = 4.3 \times 10^{16}$ , while at 1327°,  $\Delta F^0 = -24,528$  and  $K = 2.2 \times 10^8$ .

**Activities.** Activities have been discussed on pages 292 and 460, and it has been emphasized that the mass law and the laws of thermodynamics may be applied with exactness when activities  $a$  are used.

Formulas involving activities were derived, but when these formulas were applied to practical problems concentrations were often substituted for activities. The results were only approximately correct except in very dilute solutions where the activities and the concentrations are essentially equal. In some cases activity coefficients were



arbitrarily given, so that concentrations could be converted into activities. It is the purpose of this section to show how activities may be determined experimentally.

A good illustration of the need of activities in thermodynamical calculations is shown in the determination of the dissociation constant at  $25^\circ$  of  $\text{N}_2\text{O}_4$ , at different total concentrations,\* as shown in Fig. 131.

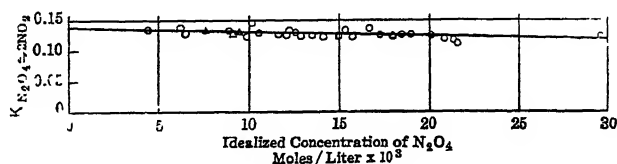


FIG. 131

If  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  behaved as perfect gases, the law of concentration effect should hold exactly and the values of the dissociation constant, calculated from  $K_p = p_{\text{NO}_2}^2/p_{\text{N}_2\text{O}_4}$ , should be independent of the concentration of material. Then when  $K_p$  is plotted against the total concentration of material, a horizontal line should be produced. It is evident from Fig. 131, however, that  $K_p$  increases as the total pressure is reduced. The increase is about 13 per cent for a change of 1 atm. In the derivation of the relation,  $\Delta F^\circ = -RT \ln K$ , it is assumed that the gases are ideal gases, and accordingly the correct value to use in thermodynamical calculations is the value extrapolated to zero pressure where the gases are strictly ideal. In this case  $K$  has a value of 0.143 at zero pressure. Sometimes it is possible in this way to obtain a correct equilibrium constant or a standard electrode potential by extrapolation to infinite dilution without direct determination of the activities. More often it is necessary to obtain the activities by reference to some standard state.

At a definite temperature a pure liquid has a definite tendency to pass off into the vapor state; this tendency is measured by its vapor pressure  $p_0$ . When a solute is added, the vapor pressure of the solvent  $p$  is decreased. The ratio  $p/p_0$  is a measure of the escaping tendency of the solvent as compared to the escaping tendency in the pure liquid. It may be considered as describing approximately the *activity* of the solvent. For example, the vapor pressure of pure water at  $25^\circ$  is 23.7, and the partial pressure of water in a 10 per cent solution of sulfuric acid is 22.4. Then the relative escaping tendency or activity in solution is  $22.4/23.7$  or 0.95. This relation is not exact, however.

\* Verhoek and Daniels, *J. Am. Chem. Soc.*, **53**, 1250 (1931).

because the deviations of the vapors from the perfect gas laws introduce another variable.

There is a great practical advantage to be gained by utilizing the perfect gas laws, and in order to apply these laws to ordinary gases, G. N. Lewis invented the term *fugacity*,  $f$ , which is related to the free energy by the equation

$$F = RT \ln f + C \quad [12]$$

where  $F$  is the free energy per mole and  $C$  is a constant at a given temperature. Fugacity is a corrected pressure so defined as to make the thermodynamical equations apply with exactness.\* Likewise when the gas is in its standard state

$$F^0 = RT \ln f^0 + C \quad [13]$$

and subtracting

$$F - F^0 = RT \ln \frac{f}{f^0} \quad [14]$$

The term  $F - F^0$  represents the change in free energy on passing from the standard state in which the fugacity is  $f^0$  to the specified state where it is  $f$ .

Referring to the preceding page, the activity  $a$  is defined approximately by the relation

$$a = \frac{p}{p^0} \quad [15]$$

but it is defined exactly by the equation

$$a = \frac{f}{f^0}$$

This leads to the equation

$$F - F^0 = RT \ln a \quad [16]$$

and for small changes at constant temperature

$$dF = RT da \quad [17]$$

When the substance is in its standard state the fugacity  $f$  is equal to  $f^0$ , and  $f/f^0$  or  $a$  is unity,  $RT \ln a$  is zero, and  $F = F^0$ . Under any

\* Fugacities of gases may be calculated from pressures by correcting for the deviations from ideal behavior at several pressures, and in different ways as given by Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," Chapter XVII, McGraw-Hill Book Co., New York, 1923.

conditions the activity is defined by equation (16). The choice of a standard state is arbitrary and determined by convenience.

For gases the standard state is chosen so that at low pressures the fugacity equals the partial pressure of the gas, and the activity is equal to the fugacity. For a perfect gas it is equal to the pressure; to a good approximation at ordinary pressures of about an atmosphere or below, the activity of any gas is nearly equivalent to the pressure.

For a solvent the standard state is taken as the pure solvent and the activity  $a_1$  in a solution is given by the expression  $a_1 = f_1/f_1^0$ , where  $f_1^0$  is the fugacity of the pure solvent. In very dilute solutions where the mole fraction of the solvent,  $N_1$ , is nearly unity, the activity  $a_1$  of the solvent is nearly equal to the mole fraction and the approximate relation follows

$$f_1 = N_1 f_1^0 \quad [18]$$

Since the fugacities are practically the same as the pressures at ordinary pressures

$$p_1 = N_1 p_1^0 \quad [19]$$

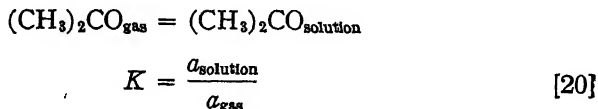
This relation is recognized as Raoult's law (page 180).

For a solute which is a liquid when pure, the standard state is usually taken as a hypothetical state in which the pure solute (i.e., a solution in which  $N_2 = 1$ ) would have the properties which the solute possesses at infinite dilution. The activity of a solute at any mole fraction is given by the expression  $a_2 = f_2/f_2^0$ .

The calculation of activities is illustrated in the following sections.

**Activities from Vapor Pressures.** In Table II the partial pressures of acetone and ether are given in millimeters at 30° for solutions of various mole fractions.\*

Considering the acetone to be the solute the standard reference state is taken as a hypothetical acetone with the properties which it possesses at infinite dilution. Writing the equilibrium constant for the reaction



The gas is sufficiently ideal so that no serious error is introduced by substituting the pressure of the gas for the activity. Since the solution is far from ideal a considerable error would be introduced by substituting the mole fraction for the activity of acetone in solution and

\* Sameshima, *J. Am. Chem. Soc.*, **40**, 1489 (1918).

TABLE II  
VAPOR PRESSURE OF ACETONE-ETHER SOLUTIONS AT 30°

Mole Fraction Ether $N_1$	Vapor Pressure Ether $p_1$	Mole Fraction Acetone $N_2$	Vapor Pressure Acetone $p_2$	$\frac{N_2}{p_2}$	Total Pressure $p_1 + p_2$
1.000	646.0	0.000	0	....	646.0
0.961	623.5	0.0387	21.8	0.00177	645.3
0.867	570.8	0.133	66.2	0.00201	637.0
0.749	510.2	0.251	106.7	0.00235	616.9
0.504	390.3	0.496	167.5		557.8
0.349	301.5	0.651	201.2		502.7
0.295	266.0	0.705	213.7		479.7
0.162	166.5	0.838	243.1		409.6
0.066	71.0	0.934	266.8		337.8
0.047	55.3	0.953	270.7		326.0
0.020	20.8	0.980	276.6		297.4
0.000	0.0	1.000	282.7		282.7

$K$  would not be the same at different concentrations. However, by writing

$$K' = \frac{N_2}{p_2} \quad [21]$$

and calculating the value of  $K'$  at several different concentrations it is possible to extrapolate back to infinite dilution where the solution

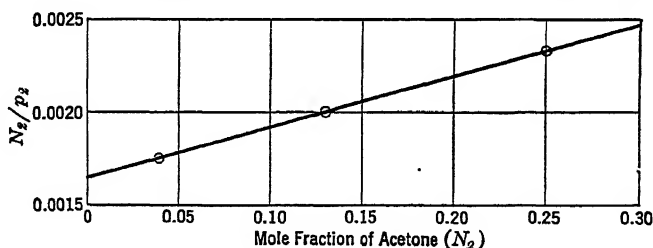


FIG. 132

is ideal. This extrapolated value of  $K'$  is the true equilibrium constant under conditions where the activity is equal to the mole fraction. This extrapolation is illustrated in Fig. 132, where it is found that  $K$  has the value 0.001697.

Since  $K$  has been evaluated it is now possible with the help of equation (20) to determine the activity of acetone at any concentration from its vapor pressure. Thus at a mole fraction of 0.251 the partial

vapor pressure is 106.7 and its activity in solution is given by the relation

$$a_2 = 0.001697 \times 106.7 = 0.181 \quad [22]$$

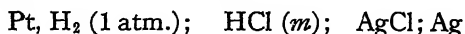
The fact that the activity of acetone is less than its mole fraction means that its escaping tendency (represented approximately by its vapor pressure) is less than if the acetone retained in this solution the properties which it possesses in an extremely dilute solution in ether.

Considering ether to be the solvent, its activity at any mole fraction is simply the ratio of the partial pressure to the vapor pressure of pure ether, which is 646.0 mm. For example, the partial pressure of ether at 0.295 mole fraction is 266.0 mm. and the activity of the ether is  $266.0/646.0$  or 0.412. If the solution were ideal the activity would be 0.295.

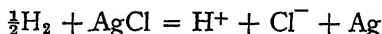
Of course it is quite arbitrary to take ether as the solvent and acetone as the solute; equally useful results would be obtained if ether were considered to be the solute. The standard state adopted should be specified, but in calculations involving only differences in concentration the standard state cancels out.

**Activities from Electromotive Force.** Any property which depends on the escaping tendency of a material in solution may be used for measuring activities. When an electrode is placed in a solution of its ions the voltage depends on the frequency with which the ions collide with the electrode and this in turn depends on the *activity* or effective concentration of the ions. The standard state could be taken as a 1 molal solution or one of any other specified concentration, but it is better to consider the standard state of the solute as a hypothetical state in which the solute at an effective concentration of 1 molal has the properties which it possesses at infinite dilution. Again it is necessary to determine some property which depends on the activity and to extrapolate to infinite dilution. The determination of activities of electrolytes may be illustrated with hydrochloric acid.

The following cell, without transference,



is reversible with respect to both electrodes, and its voltage depends on the activity of hydrochloric acid. The cell reaction is



The activity coefficient of the hydrochloric acid is represented by  $\gamma$ , and at each concentration the activity of the hydrogen ion is  $\gamma m$  and that of the chloride ion is also  $\gamma m$ , where  $m$  is the molality.

The electromotive force of the cell is given by the equation (page 441)

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{H^+} \times a_{Cl^-} \times a_{Ag}}{a_{AgCl} a_{H_2}} = E^0 - \frac{RT}{F} \ln \gamma^2 m^2 \quad [23]$$

where  $E$  is the measured potential and  $E^0$  is the standard potential, i.e., the electromotive force of the cell when the activity of hydrochloric acid is unity. Rearranging and putting in numerical values for  $25^\circ$ ,

$$E + 0.1183 \log m = E^0 - 0.1183 \log \gamma \quad [24]$$

Since at infinite dilution  $\gamma = 1$  and  $\log \gamma = 0$ , it can be seen that when  $E + 0.1183 \log m$  is plotted against  $m$ , the extrapolation of  $E + 0.1183 \log m$  to  $m = 0$  will give  $E^0$ .

In order to make a satisfactory extrapolation, use is made of the Debye-Hückel theory to furnish a function which will give nearly a straight line. From this theory is obtained the following expression for the activity coefficient of any uni-univalent electrolyte (e.g., HCl) in dilute aqueous solutions at  $25^\circ$

$$\log \gamma = -0.509 \sqrt{m} + bm \quad [25]$$

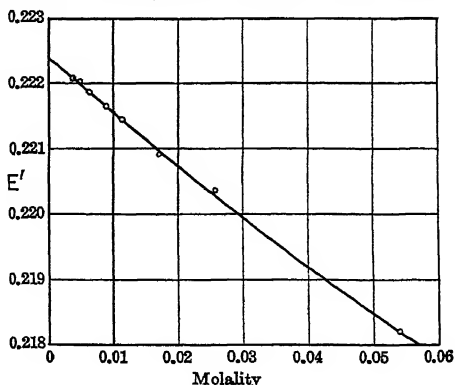
where  $b$  is an empirical constant depending partly on the radii of the ions (page 44).

Substituting in (24) and rearranging terms

$$E + 0.1183 \log m - 0.0602 \sqrt{m} = E^0 - (0.1183b)m \quad [26]$$

According to this equation the left-hand side, which we will designate as  $E'$ , will give a straight line when it is plotted against  $m$ , and its value at infinite dilution is  $E^0$ . Actually the line will be somewhat curved, since (25) is exact only in very dilute solutions, but the extrapolation of  $E'$  can usually be made without difficulty.

In Table III are given the measured electromotive forces and values of  $E'$  at various molalities, and in Fig. 133,  $E'$  is plotted against  $m$ . The extrapolated value is 0.2224 volt.



of the silver-silver chloride standard electrode potential. Similar methods have been used for calculating other standard electrode potentials.

TABLE III  
ELECTROMOTIVE FORCE OF CONCENTRATION CELLS OF HCl<sup>1</sup>

$m$	$E$	$E'$
0 003564	0 51527	0 22207
0 004488	0 50384	0 22204
0 006239	0 48747	0 22188
0 008636	0 47135	0 22162
0 011195	0 45861	0 22144
0 01710	0 43783	0 22092
0 02563	0 41824	0 22036
0 05391	0 38222	0 21820

<sup>1</sup> Harned and Ehlers, *J. Am. Chem. Soc.*, **54**, 1350 (1932).

The value of  $E^0$  having been determined, the activity coefficient of hydrochloric acid is obtained from the electromotive force of the cell for any concentration of HCl.

*Example 6.* If the electromotive force of the cell on page 526 is 0.3524 volt for  $m = 0.1$ , calculate  $\gamma$  for 0.1*m* HCl (at 25°).

$$\begin{aligned}
 0.3524 &= 0.2224 - 2 \times 0.05915 \times \log (0.1\gamma) \\
 &= 0.2224 - 0.1183 \log 0.1 - 0.1183 \log \gamma \\
 \log \gamma &= (0.2224 - 0.3524 + 0.1183) / 0.1183 = -0.0989 \\
 \gamma &= 0.796
 \end{aligned}$$

**Activities of Solvent from Activities of Solute.** In a binary mixture  $N_1 + N_2 = 1$ , where  $N_1$  refers to the mole fraction of the solvent and  $N_2$  refers to the mole fraction of the solute, and

$$dN_1 = -dN_2 \quad [27]$$

but since  $d \ln N = dN/N$

$$N_1 d \ln N_1 = -N_2 d \ln N_2 \quad [28]$$

Furthermore, it can be shown that for changes in concentration in binary mixtures at constant temperature and pressure, the free energy  $F$  (or any additive property) is governed by the equation  $N_1 dF_1 + N_2 dF_2 = 0$ . Rearranging

$$dF_1 = -\frac{N_2}{N_1} dF_2 \quad [29]$$

Substituting in this equation  $RT d \ln a$  for  $dF$  as given in equation (17)

$$d \ln a_1 = - \frac{N_2}{N_1} d \ln a_2 \quad [30]$$

Subtracting equation (28) from equation (30)

$$d \ln \frac{a_1}{N_1} = - \frac{N_2}{N_1} d \ln \frac{a_2}{N_2} \quad [31]$$

At infinite dilution the solution is essentially the same as the solvent and then the activity  $a_1^0$  of the solvent is practically the same as the mole fraction  $N_1$ . Then,

$$\frac{a_1^0}{N_1^0} = 1 \quad \text{and} \quad \log \frac{a_1^0}{N_1^0} = 0$$

and integrating equation (31) between infinite dilution and some specified mole fraction,

$$\log \frac{a_1}{N_1} = - \int_0^{N_2} \frac{N_2}{N_1} d \log \frac{a_2}{N_2} \quad [32]$$

Now the integral on the right-hand side of the equation may be determined if the relation is known between  $N_2/N_1$  and  $\log a_2/N_2$ ; or it may be evaluated graphically by plotting  $N_2/N_1$  against  $\log a_2/N_2$  and finding the area under the curve.

This method\* can be used to determine the activities of mercury in a thallium amalgam at 20° from a knowledge of the activities of thallium as illustrated in Fig. 134. The activities of thallium in mercury solutions were readily obtained by measuring the potential difference between two amalgams of different concentration in contact with a solution of thalious sulfate. The measurements were carried to low concentrations and then the value of  $E^0$  was determined by extrap-

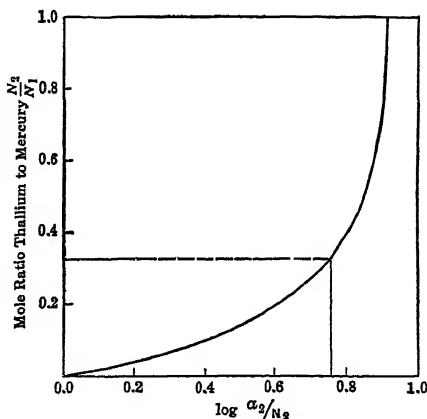


FIG. 134

\* Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 233 (1921); "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 269



olation in a manner similar to that described for hydrochloric acid. In Table IV the activities of thallium obtained in this way, at various mole fractions, are divided by the mole fractions and shown in the fourth column.

In Fig. 134 a dotted line is shown corresponding to a mole fraction of thallium of  $\frac{1}{4}$  (mole ratio of  $\frac{1}{3}$ ), and the activity of the mercury at this concentration is readily obtained after measuring the area under the curve out to the intersection with this dotted line. This area,  $\int_0^{0.25} \frac{N_2}{N_1} d \log \frac{a_2}{N_2}$ , is equal to  $-\log a_1/N_1$ , from which  $a_1/N_1$  and  $a_1$  may be calculated readily. The data of the last two columns were obtained by this method, carrying out the graphical integration to different limits.

TABLE IV  
ACTIVITIES OF MERCURY IN THALLIUM AMALGAMS

Mole Fraction Thallium $N_2$	Mole Fraction Mercury $N_1$	Mole Ratio $N_2/N_1$	Activity Tl	Activity Hg	Activity Hg $a_1$
			Mole Fract. Tl $a_2/N_2$	Mole Fract. Hg $a_1/N_1$	
0	1	0	1	1	1
0.005	0.995	0.00502	1.06	0.9998	0.995
0.01	0.99	0.0101	1.15	0.999	0.989
0.05	0.95	0.0526	1.80	0.986	0.937
0.1	0.90	0.111	2.84	0.950	0.855
0.2	0.80	0.250	4.98	0.866	0.693
0.3	.....	.....	6.60	.....	<i>y</i>
0.4	0.60	0.666	7.57	0.734	0.440
0.5	0.50	1.000	7.98	0.704	0.352

A similar method can be used for calculating the activity of the solute from that of the solvent, but here the curve approaches the axis asymptotically and the determination of the area is inaccurate. It is more satisfactory, then, to plot some arbitrary function of the activity of the solvent which approaches zero at infinite dilution. Such a method is particularly valuable in aqueous solutions where the activity of the solvent may be determined easily.

**Activities from Freezing Points.** The activity of water is diminished by the addition of a solute, and this lessening of the escaping tendency leads to a lowering of the freezing point. Since freezing-point depressions can be measured more accurately than the other colligative properties of solutions they are often used for determining the activities of the solvent and, with an equation similar to (32), they are used also

for determining the activities of the solute. In an earlier chapter (page 212) it was shown that the concentration of a solute can be calculated approximately in a dilute solution when the freezing point of the solution and that of the solvent are known; but in calculating activities with precision it is necessary to know the freezing points not only of solutions of the specified concentrations but also of several additional concentrations out to extreme dilutions. The following equations can be obtained from earlier pages, and with the proper substitutions it is possible to obtain a working equation from which activity coefficients can be obtained from molalities partly by graphical integrations. Application of the Clapeyron equation (page 154) to the vapor pressure of ice  $p_s$  and of pure supercooled water  $p_l$  at the same temperature gives

$$\frac{d \ln (p_s/p_l)}{dT} = \frac{\Delta H_s - \Delta H_v}{RT^2} = \frac{\Delta H_f}{RT^2} \quad [33]$$

where the  $\Delta H$  values are the heats of sublimation, vaporization, and fusion, respectively. Strictly speaking, fugacities rather than pressures should be used, but the pressures are low enough to be nearly equal to the fugacities.

At the freezing point of the solution the vapor pressure,  $p_1$ , of the solution equals  $p_s$ . By choosing pure liquid water as the standard state at any temperature, so that the activity of water in the solution is  $a_1 = p_1/p_l$ , the following equation results.

$$\frac{d \ln a_1}{dT} = \frac{d \ln p_1/p_l}{dT} = \frac{d \ln p_s/p_l}{dT} = \frac{\Delta H_f}{RT^2} \quad [34]$$

Assuming that  $\Delta H_f$  is constant and integrating between the limits  $T$ , the freezing point of the solution, and  $T_0$ , the freezing point of pure water, where  $a_1 = 1$

$$\ln a_1 = \frac{-\Delta H_f (T_0 - T)}{R T T_0} \cong \frac{-\Delta H_f}{R T_0^2} \Delta T_f \quad [35]$$

the last term being a good approximation when  $\Delta T_f$  or  $T_0 - T$  is small. This equation relates the activity of water in a solution to the freezing point depression. It gives the activity at the freezing point of the solution, but the activities in a solution of given concentration are so nearly independent of temperature if the solution is dilute that  $a_1$  can be considered as the activity of water in the solution at a specified temperature, say  $25^\circ$ .

When the concentration is changed at constant temperature and pressure,

$$d \ln a_1 = \frac{-N_2}{N_1} d \ln a_2 \quad [36]$$

where  $a_2$  is the activity of  $N_1$  the solute.

The corresponding change in  $\Delta T_f$  will be given by differentiation of (35)

$$d \ln a_1 = \frac{-\Delta H_f}{RT_0^2} d(\Delta T_f) \quad [37]$$

The activity  $a_2$  of an electrolyte of type  $A_xB_y$  is related to the activity coefficient  $\gamma$  and molality  $m$  by

$$a_2 = (\gamma \times xm)^x (\gamma \times ym)^y = (\gamma m)^\nu x^x y^y \quad [38]$$

where  $\nu = x + y$  is the number of ions per molecule. Thus for  $\text{BaCl}_2$

$$a_2 = (\gamma m)(\gamma \times 2m)^2 = (\gamma m)^3 \times 4$$

Taking logarithms in equation (38) and differentiating

$$d \ln a_2 = \nu d \ln \gamma + \nu d \ln m \quad [39]$$

and combining equations (36), (37), and (39)

$$\nu d \ln \gamma + \nu d \ln m = \frac{N_1}{N_2} \frac{\Delta H_f}{RT_0^2} d(\Delta T_f) = \frac{d \Delta T_f}{1.858m} \quad [40]$$

Numerical values for water are used to give  $1.858m$  in the last term.

Graphical integration of a plot of  $1/1.858m$  against  $\Delta T_f$  can be used to evaluate relative values of  $\gamma$  with the aid of this equation, but since  $1/m$  becomes infinite at  $m = 0$  the equation is not convenient for extrapolation to infinite dilution. To avoid this difficulty the  $j$  function is introduced as follows.

$$j = 1 - \frac{\Delta T_f}{1.858\nu m} \quad [41]$$

Since  $\Delta T_f/m$  approaches  $1.858\nu$  in dilute solution,  $j$  approaches zero for  $m = 0$ .

Differentiating,

$$\begin{aligned} dj &= \frac{-d \Delta T_f}{1.858\nu m} + \frac{\Delta T_f}{1.858\nu m^2} dm \\ &= \frac{-d \Delta T_f}{1.858\nu m} + (1 - j) \frac{dm}{m} \end{aligned} \quad [42]$$

Substituting for  $d \Delta T_f / 1.858m$  in (40) and rearranging,

$$d \ln \gamma = -dj - j \frac{dm}{m} \quad [43]$$

Integrating between concentrations 0 and  $m$  we get the final working equation,

$$\ln \gamma = -j - \int_0^m j \frac{dm}{m} \quad [44]$$

where  $\gamma$  is the activity coefficient at the molality  $m$ . The last quantity in this equation can be obtained by graphical integration of a plot of  $j/m$  against  $m$ .

In accurate work corrections can be made for the approximations made in this treatment, such as the change in  $\Delta H$  and  $a_1$  with temperature.

Further material on the determination of activities from freezing-point measurements may be found in the literature.\*

**Partial Molal Quantities.** The concept of partial molal quantities, developed by G. N. Lewis, has helped materially in placing the study of solutions on an exact basis. For example, when a mole (32 g.) of methyl alcohol is added to a small quantity of water the change in volume produced on mixing is not the same as when the alcohol is added to a large quantity of water. The volume depends on the concentration, and since the concentration changes during the mixing the measurements are complicated in a manner which was not realized in the early work on solutions. This problem can be solved readily with the methods of partial differentiation by determining the change produced by the addition of an infinitesimal quantity of the solute. The partial molal volume  $\bar{V}$  is defined so that

$$\bar{V} = \frac{\partial V}{\partial n} \quad [45]$$

where  $n$  is the number of moles. It is the rate of change in volume produced by the addition of solute to the solution at constant temperature, pressure, and concentration. The partial molal volume of the solute  $\bar{V}_2$  changes with the concentration, and it can be visualized as the increase in volume produced by adding 1 mole of the solute to a

\* Randall and Vanselow, *J. Am. Chem. Soc.*, **46**, 2418 (1924); Scatchard, *J. Am. Chem. Soc.*, **47**, 648 (1925); Scatchard and Benedict, *J. Am. Chem. Soc.*, **58**, 837 (1936); Getman, *J. Phys. Chem.*, **34**, 1454 (1930); Robertson and LaMer, *J. Phys. Chem.*, **35**, 1953 (1931).

large quantity of the solution, a quantity so large in fact that the addition of the 1 mole of solute does not increase appreciably the concentration of the solution. For example, a mole of methanol weighs 32.03 g. and occupies 40.45 ml. When it is added to a large reservoir of pure methanol the volume is increased 40.45 ml., but when it is added to a large reservoir of a solution containing 0.2 mole fraction of methanol and 0.8 mole fraction of water the increase is only 37.7 ml. An obvious method for determining the partial molal volume of a solute consists in plotting the volume of the solution against the number of moles of solute contained in 1000 g. of the solvent (i.e., against the molality), and determining the slope of the curve as

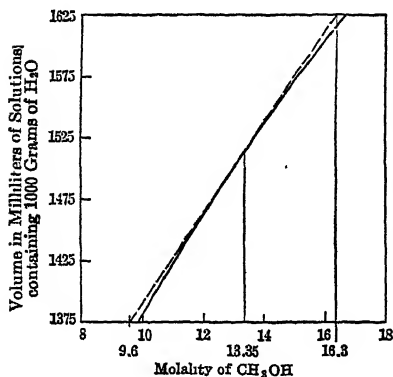


FIG. 135

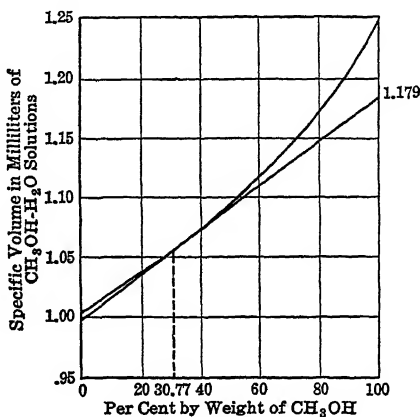


FIG. 136

shown in Fig. 135. The slope of the curve  $\partial V/\partial n_2$  at any molality gives the rate of change in volume with the moles of solute added, and this is by definition the partial molal volume of the solute. In Fig. 135 the tangent is drawn to the curve at a molality of 13.35, corresponding to a mole fraction of 0.20, and it is found to have a slope of  $(1625 - 1375)/(16.30 - 9.60)$  or 37.3, which is the partial molal volume of the methanol at this molality.

The method just given illustrates the meaning of the partial molal quantities, but it is possible to obtain greater accuracy by other methods.

The *method of intercepts* is illustrated in Fig. 136 where the specific volume (the volume of 1 g. of the solution, or the reciprocal of the density) is plotted against the percentage by weight. It can be shown that when a tangent is drawn the intercepts on the extreme ordinates give at once the partial specific volumes of the two components in the

solution at the composition corresponding to the point of tangency.\* The partial specific volumes are converted into partial molal volumes by merely multiplying by the molecular weights.

The data and calculations on which Fig. 136 is based are given in Table V.

TABLE V  
PARTIAL MOLAL VOLUMES OF METHANOL AND WATER  
Method of Intercepts

Mole Fraction CH <sub>3</sub> OH	Percentage CH <sub>3</sub> OH	Density Solution	Specific Volume	Molal Volume	Partial Molal Volume	
					H <sub>2</sub> O	CH <sub>3</sub> OH
0	0	0.9982	1.002	18.05	.....	.....
0.20	30.77	0.9503	1.053	21.93	18.0	37.8
0.40	54.24	0.9068	1.103	26.05	17.3	39.0
0.60	72.73	0.8647	1.157	30.56	16.7	39.8
0.80	87.66	0.8268	1.210	35.34	15.3	40.4
1.00	100.0	0.7917	1.263	40.45	.....	.....

A tangent is drawn at a composition of 30.77 per cent (mole fraction = 0.20), and it intersects the ordinates at 0.9973 and 1.1795.

The partial molal volume of water is  $18.02 \times 0.9973 = 18.0$ , and that of methanol is  $32.03 \times 1.1795 = 37.7$ , a value which agrees within the errors of graphing on a small scale with that obtained by the other method shown in Fig. 136, namely, 37.3.

Other properties such as partial molal free energy or partial molal heat capacities or partial molal heat contents may be determined in the same way as the partial molal volumes. The partial molal free energy  $\bar{F}$  of a given component is an important quantity which is used in deriving formulas for the thermodynamic behavior of solutions because it has the same value in every phase which is in equilibrium.

After the partial molal volumes (or other properties) have been determined, the volume of the whole solution can be obtained at any concentration by direct addition, as shown by the equation

$$n_1\bar{V}_1 + n_2\bar{V}_2 + n_3\bar{V}_3 + \cdots = V \quad [46]$$

where  $V$  is the volume of the whole solution, and where  $n_1$ ,  $n_2$ ,  $n_3$ , etc.,

\* Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 38.

refer to the number of moles of the different components and  $\bar{V}$  to the corresponding partial molal volumes. (Column 5 of Table V.)

**The Third Law of Thermodynamics.** The first law of thermodynamics is concerned with conservation of energy and the second law with the relation between heat and work. The third law is concerned with entropy and means of evaluating it in absolute terms. The first and second laws were discussed in Chapters V and VII and the concept of entropy was introduced in Chapter VII.

In chemical thermodynamics, with which we are concerned in this chapter, the important equations are

$$\Delta F^0 = -RT \ln K \quad [47]$$

$$\Delta F = \Delta H - T\Delta S \quad [48]$$

$$\Delta F = \Delta H_0 - \Delta F_0 T \ln T - \frac{1}{2} \Delta F_1 T^2 \cdots + IT \quad [49]$$

According to the *third law of thermodynamics*, the entropy of most crystals at the absolute zero may be taken as zero. This law is important, for it makes possible the determination of absolute entropies. The increase in entropy involved in heating from absolute zero to any specified temperature may be calculated with the help of equation (50) derived on page 131,

$$S = \int_0^T C d \ln T \quad [50]$$

and according to the third law this increase in entropy is the absolute entropy. Tables of entropy have been prepared from specific heat data, and from these entropies the entropy changes in chemical reactions can be determined from the relation  $\Delta S = S_{\text{products}} - S_{\text{reactants}}$ .

Combining these data with heats of reaction, one can calculate free energy changes and equilibrium constants at various temperatures, using equations (48) and (47).

It has been indicated that the greater the randomness of a system the greater is the entropy  $S$ . A crystal with its orderly arrangement of atoms in the crystal lattice should have a comparatively small entropy content. Moreover, the random motion of atoms and molecules, due to heat, decreases as the temperature is lowered and the entropy must decrease greatly as the absolute zero is approached.

There is as yet no conclusive proof of the validity of the third law, but it has been checked and cross-checked in many different ways. In the following section, for example, it will be shown that the entropy calculations based on the third law agree well with the entropy values as calculated from measurements of free energy and heat content.

The first idea on which the third law is based was suggested in 1902 by Richards, who found that the temperature coefficient of voltage of most galvanic cells approached zero at low temperatures. It was developed by Nernst. More recent developments have been due to Lewis† and his associates, Eucken, Parks,‡ Giauque,§ Aston,|| and others. The theory of the subject has been treated fully by Aston.||

The determination of absolute entropies is illustrated with the data on silver shown in part in Table VI and plotted in Fig. 137.

TABLE VI  
HEAT CAPACITY OF SILVER\*

$T$	$\log T$	$C_v$	$T$	$\log T$	$C_v$
15	1.1761	0.160	140	2.1461	5.310
20	1.3010	0.410	160	2.2041	5.461
25	1.3979	0.747	180	2.2553	5.584
30	1.4771	1.140	200	2.3010	5.653
40	1.6021	2.001	220	2.3424	5.708
60	1.7782	3.405	240	2.3802	5.765
80	1.9031	4.245	260	2.4150	5.819
100	2.0000	4.769	280	2.4472	5.843
120	2.0792	5.092	298.1	2.4744	5.851
			300	2.4771	5.852

Taking the entropy at 0° K. as zero, according to the third law, and applying equation (50), the absolute entropy at 298.1° K. is given by the equation

$$S_{298} = 2.303 \int_0^{298.1 \text{ K.}} C d \log T \quad [51]$$

The theoretical relation between  $C$  and  $\log T$  is not known (except at very low temperatures), and so it is necessary to evaluate the integral by graphical means. The area ( $\int y dx$ ) is determined by plotting accurately  $C_v$  against  $\log T$  and counting the squares under the curve out to  $\log 298.1$  K., this area in turn being multiplied by the conversion factor of natural logarithms. For silver, the value of  $S_{298.1 \text{ K.}}$  obtained by evaluating this area is 10.21 entropy units (calories per degree).

\* Meads, Forsythe, and Giauque, *J. Am. Chem. Soc.*, **63**, 1902 (1941).

† Lewis, Gibson, and Latimer, *J. Am. Chem. Soc.*, **44**, 1008 (1922).

‡ Parks, and co-workers, *J. Am. Chem. Soc.*, **47**, 338 (1925); **48**, 1506, 2788 (1926); **52**, 1032, 1547, 3241, 4381 (1930); and later articles.

§ Giauque and Blue, *J. Am. Chem. Soc.*, **58**, 831 (1936).

|| Aston, in Taylor and Glasstone, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1942, Chapter IV.



Specific heat measurements have been made with special electrical calorimeters on many substances down to liquid air temperatures, and on some substances down to the boiling point of hydrogen, and lower. The extrapolation to absolute zero does not involve very large errors, and fortunately, in the region of absolute zero, the specific heat-temperature curve can be calculated with fair accuracy from formulas\* which rest partly on theoretical foundations.

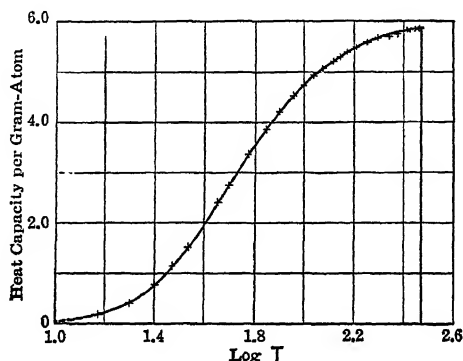


FIG. 137

An increase in entropy is produced by mixing two substances, and if the entropy of these pure substances is zero at  $0^{\circ}$  K. the mixture cannot be zero also. Accordingly the third law is restricted to pure crystals, but often it may be applied, with only small errors,† to solutions and glasses.

If there is a change of state, or a transition from one crystalline form to another, the heat absorbed in the change must be divided by the temperature at which the change takes place, and added to the entropy as calculated from the specific-heat curve.

Table VII gives the absolute entropies at constant pressure of one atmosphere for a number of elements and compounds obtained from these specific-heat measurements at low temperatures.

**Thermodynamical Calculations of Equilibrium Constants.** The relation between the entropy change and free energy change in an

\* Einstein, *Ann. Physik*, [4] **22**, 180 (1907); Debye, *ibid.*, [4] **39**, 789 (1912).

† An interesting case is that of hydrogen, which exists in two forms, ortho and para, having different specific heats as described in Chapter XIX. Thermodynamical calculations persisted in showing that the entropy of hydrogen was too low by an appreciable amount, and it is now known that an entropy increase of this magnitude due to the change from one form to the other, does actually occur just above the absolute zero. The change comes at such a low temperature in the case of hydrogen that it was missed in the early experimental measurements.

TABLE VII

ATOMIC AND MOLECULAR ENTROPIES AT 25°

Water ( <i>l</i> )	16.8	Methane ( <i>g</i> )	44.5
Hydrogen ( $\frac{3}{2}\text{H}_2$ ) ( <i>g</i> )	15.6	Methanol ( <i>l</i> )	30.3
Carbon (diamond)	0.6	Maleic acid ( <i>s</i> )	38.1
Carbon (graphite)	1.4	Fumaric acid ( <i>s</i> )	39.7
Nitrogen ( $\frac{5}{2}\text{N}_2$ )	22.9	Benzene ( <i>l</i> )	41.9
Oxygen ( $\frac{3}{2}\text{O}_2$ )	24.5	Ethanol ( <i>l</i> )	38.4
Helium ( <i>He</i> )	29.8	<i>tertiary</i> -Butanol ( <i>l</i> )	45.3
Sulfur (rhombic)	7.6	<i>cyclo</i> -Hexane ( <i>l</i> )	49.2
Sulfur (monoclinic)	7.8	Toluene ( <i>l</i> )	52.4
Chlorine ( $\frac{3}{2}\text{Cl}_2$ ) ( <i>g</i> )	26.6	<i>n</i> -Butanol ( <i>l</i> )	54.5
Silver ( <i>s</i> )	10.2	<i>n</i> -Hexane ( <i>l</i> )	70.6
Mercury ( <i>l</i> )	17.8	Ethylbenzene ( <i>l</i> )	61.2
Hydrochloric acid ( <i>g</i> )	44.7	Ethyl ether ( <i>l</i> )	60.5
Carbon dioxide ( <i>g</i> )	51.1	<i>n</i> -Heptane ( <i>l</i> )	78.6
Copper ( <i>s</i> )	8.0	Ethylene ( <i>g</i> )	52.5
Lead ( <i>s</i> )	15.5	Acetylene ( <i>g</i> )	48.0

isothermal reaction was given in equation (48), thus

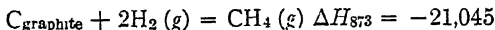
$$\Delta F = \Delta H - T \Delta S$$

It is evident that when there is no change in entropy during a reaction the change in heat content is equal to the change in free energy. Usually, however, there is an entropy change during the reaction and the decrease in free energy is greater or less than the decrease in heat content depending on the sign of  $\Delta S$ .

Since entropies and heats of reaction can be determined from calorimetric measurements alone, it is now possible to calculate free energy changes and equilibrium constants without involving any chemical measurements. This determination of chemical affinities from thermal data is a goal which was eagerly sought by many early investigators.

The calculation of chemical equilibria from entropy data using equations (48) and (47) is particularly valuable in organic chemistry because frequently no other method is available. Often the reaction rates are so very slow that direct measurements of equilibrium are impossible. Methane may be taken as an example. Methane appears to be a stable substance at room temperature, and carbon and hydrogen appear to be unreactive toward each other. It is not possible then to measure the equilibrium among the three at low temperatures, but it may be determined indirectly from the entropies and the heat of reaction.

*Example 6.* Calculate from thermal data alone the equilibrium constant of the following reaction at 600° C.,



The entropies of  $\text{C}_{\text{graphite}}$ ,  $\text{H}_2$ , and  $\text{CH}_4$  are 4.8, 38.9, and 56.6 respectively at 873° K. and 1 atm.

$$\Delta S = S_{\text{products}} - S_{\text{reactants}} = 56.6 - (38.9 \times 2 + 4.8) = -26.0$$

$$\Delta F^0 = \Delta H - T \Delta S = -21,045 - [873 \times (-26)] = 1653$$

Since

$$\Delta F^0 = -RT \ln K$$

$$K = 0.386$$

This method of calculating equilibrium constants from entropy data has come into extensive industrial use, particularly in determining whether or not a given synthesis is thermodynamically possible.

The limiting factor in many calculations of this type is the low accuracy with which the heats of reactions are known. These values are usually obtained from differences between large quantities, and a small error in one of these values makes a large error in the value of  $\Delta F$ . In the calculation of the methanol equilibrium, for example, an error of 0.1 per cent in one of the values for the heat of combustion makes an error of 35 per cent in the equilibrium constant. For a time the validity of the third law itself was questioned because of the large discrepancy between the calculated and observed equilibrium in the methanol synthesis. This discrepancy was finally traced to a considerable error in the heat of combustion of methanol. As a rule, a greater error can be tolerated in the entropy measurements than in the measurements which determine the values of the heat content.

Many new measurements of entropies and free energies are being recorded in the current literature and tables of reliable data will ultimately make possible the calculation of most equilibrium constants. Parks and Huffman\* gave an excellent collection of the data for organic compounds available up to 1932, together with theoretical discussions and examples of the use of these data. A very helpful collection of data and techniques for calculating thermodynamic data has been written by Wenner.† Semi-empirical and theoretical methods are given for estimating specific heat and other important constants from meager data.

\* Parks and Huffman, "Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932.

† Wenner, "Thermochemical Calculations," McGraw-Hill Book Co., New York, 1941.

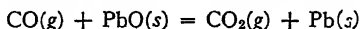
When data are not available for certain compounds it is still possible to estimate free energies and entropies, using empirical rules based on the molecular structures. For example, when  $\text{CH}_3$  is substituted for a hydrogen atom, attached to a chain, the molar free energy of formation at  $25^\circ$ ,  $\Delta F^\circ_{298\text{K}}$ , is increased by about 1900 cal.; when  $\text{C}_2\text{H}_5$  is substituted it is increased by 3000 cal. In a similar way the substitution of a hydrogen atom by an OH group to form a primary alcohol gives a change in  $\Delta F^\circ_{298\text{K}}$  of  $-34,000$ ; Cl for H gives a change of  $-1600$ ;  $\text{NH}_2$  for H gives a change of 6000; and  $\text{NO}_2$  for H gives a change of 7000. For example, if  $\Delta F^\circ_{298\text{K}}$  of  $\text{C}_2\text{H}_6$  is known to be  $-10,700$ ,  $\Delta F^\circ_{298\text{K}}$  of  $\text{C}_2\text{H}_5\text{OH}$  should be about  $(-10,700 - 34,000)$ , or  $-44,700$ . Experimental measurements give  $-40,200$  cal.

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## PROBLEMS

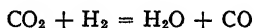
1. From the table of free energies of formation state whether the reaction



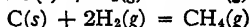
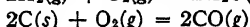
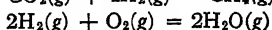
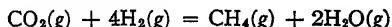
can proceed at  $25^\circ$ , and calculate the equilibrium constant.

*Ans.* Yes.  $K = 1.0 \times 10^{12}$ .

2. Determine (a)  $\Delta F^\circ$  and (b) the equilibrium constant at  $298^\circ \text{K}$  for the reaction



from the following data:



$$\Delta F^\circ_{298\text{K}} = -26,912$$

$$\Delta F^\circ_{298\text{K}} = -109,014$$

$$\Delta F^\circ_{298\text{K}} = -65,020$$

$$\Delta F^\circ_{298\text{K}} = -12,206$$

*Ans.* (a) 7,291. (b)  $4.5 \times 10^{-6}$ .

3. In a study of the formation of methane from hydrogen and graphite Storch used the following data:

$$\text{For hydrogen (H}_2\text{)} \quad C_p = 6.85 + 0.00028T + 0.00000022T^2 \\ S_{298\text{K.}} = 31.23$$

$$\text{For graphite (C)} \quad C_p = 1.22 + 0.00489T - 0.00000111T^2 \\ S_{298\text{K.}} = 1.3$$

$$\text{For methane (CH}_4\text{)} \quad C_p = 4.38 + 0.01417T \\ S_{298\text{K.}} = 43.39$$

(a) Calculate the entropies of each of these substances at 873° K. at constant pressure.

(b) Calculate  $\Delta S^\circ_{873\text{K}}$  for the reaction



*Ans.* (a) Hydrogen,  $S_{873\text{K.}} = 38.8$ ; graphite,  $S_{873\text{K.}} = 5.0$ ; methane,  $S_{873\text{K.}} = 56.3$ .

(b) -26.3 cal. per deg.

4. (a) From the data of the preceding problem calculate  $\Delta C_p$  for the reaction



(b) Find an equation expressing  $\Delta H^\circ$  as a function of temperature.  $\Delta H^\circ_{298\text{K.}}$  for this reaction is -18,062 cal. What is the value of  $\Delta H^\circ_0$ ?

(c) Calculate  $\Delta H^\circ$  for the reaction at 873° K.

$$\text{Ans. (a) } \Delta C_p = -10.54 + 0.00872T + 0.00000067T^2.$$

$$(b) \Delta H^\circ = \Delta H^\circ_0 - 10.54T + 0.00436T^2 + 0.00000022T^3.$$

$$\Delta H^\circ_0 = -15.313. \quad (c) \Delta H^\circ_{873\text{K.}} = -21,045.$$

5. (a) Using the equation for  $\Delta H^\circ$  and the value of  $\Delta H^\circ_0$  from the preceding problem, give an equation expressing  $\Delta F^\circ$  as a function of temperature.  $\Delta F^\circ_{298\text{K.}} = -11,994$  cal. What is the value of  $I$ ?

(b) Calculate  $\Delta F^\circ_{873\text{K.}}$

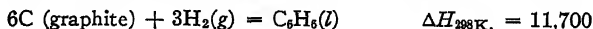
(c) Calculate  $K_p$  for the reaction  $\text{C}_{(\text{graphite})} + 2\text{H}_2(\text{g}) = \text{CH}_4(\text{g})$  at 873° K. from the free energy value of (b).

$$\text{Ans. (a) } \Delta F^\circ = -15,313 + 10.54T \ln T - 0.00436T^2 - 0.00000011T^3 + IT \\ I = -47.6$$

$$(b) \Delta F^\circ_{873\text{K.}} = 2100. \quad (c) K_p \text{ at } 873^\circ \text{ K.} = 0.30.$$

6. Using the values of  $\Delta H^\circ_{873}$  and  $\Delta F^\circ_{873}$  obtained from Problems 4 and 5 respectively, calculate  $\Delta S^\circ_{873\text{K.}}$  for the formation of methane from hydrogen and graphite. Compare the result with Problem 3(b). *Ans.* -26.4 cal. per deg.

7. Calculate the equilibrium constant for the following reaction at 25°.



having given from specific-heat measurements down to absolute zero that  $S_{(\text{graphite})} = 1.4$ ,  $S_{\text{C}_6\text{H}_6(\text{l})} = 41.9$  and  $S_{\text{H}_2} = 31.1$  at 25°. *Ans.*  $2.3 \times 10^{-22}$ .

8. When 32 g. rhombic sulfur is oxidized the evolution of heat is 82 cal. less than when 32 g. of monoclinic sulfur is oxidized. The entropy of rhombic sulfur is 7.6 eu. and that of monoclinic sulfur is 7.8 eu.

(a) What is the free energy change involved when 32 g. of monoclinic sulfur is vaporized at the vapor pressure of monoclinic sulfur at 25°, changed to vapor at the vapor pressure of rhombic sulfur and then condensed to solid rhombic sulfur at 25°?

(b) What is the ratio of the vapor pressure of rhombic to that of monoclinic sulfur?

$$\text{Ans. (a) } -22.4 \text{ cal. (b) } 0.963.$$

9. Rhombic and monoclinic sulfur exist in a state of equilibrium at the transition temperature  $95^\circ$ . Calculate  $\Delta F$  for the transition from monoclinic into rhombic sulfur at  $25^\circ$ .

For rhombic sulfur  $C_p = 4.12 + 0.0047T$

For monoclinic sulfur  $C_p = 3.62 + 0.0072T$

$$\Delta H_{295} = -82 \text{ cal.}$$

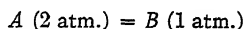
*Ans.*  $-17.6^*$

10. From the following table of densities at  $25^\circ$ , find by the method of intercepts the partial molal volumes of nitric acid and of water in (a) 20 per cent, and (b) 70 per cent solutions.

HNO <sub>3</sub> , %	Density $25^\circ$	HNO <sub>3</sub> , %	Density $25^\circ$
0	0.9997	60	1.3600
10	1.0523	70	1.4061
20	1.1123	80	1.4439
30	1.1763	90	1.4741
40	1.2417	100	1.5040
50	1.3043		

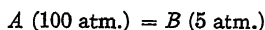
$$\begin{aligned} \text{Ans. (a) } \bar{V}_{\text{H}_2\text{O}} &= 0.9984 \times 18.02 = 17.99 \text{ ml.} & (b) \bar{V}_{\text{H}_2\text{O}} &= 15.55 \text{ ml.} \\ \bar{V}_{\text{HNO}_3} &= 0.5049 \times 63.02 = 31.82 \text{ ml.} & \bar{V}_{\text{HNO}_3} &= 40.65 \text{ ml.} \end{aligned}$$

11. The reaction  $A(g) = B(g)$  is at equilibrium when  $A$  has a partial pressure of 10 atm. and  $B$  has a partial pressure of 1 atm. Calculate: (a)  $K$ , (b)  $\Delta F^\circ$ ; (c) calculate  $\Delta F$  for the reaction



Is the reaction spontaneous or not?

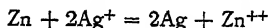
(d) Calculate  $\Delta F$  for the reaction



Is the reaction spontaneous or not?

12. Estimate with the help of data given in Example 5 at what temperature hydrochloric acid gas at a pressure of 2 atm. will be dissociated to the extent of 10 per cent.

13. From a table of free energies of formation calculate (a)  $\Delta F^\circ$ , (b) the equilibrium constant, and (c) the voltage of the cell corresponding to the reaction at  $25^\circ$ :



14. The free energy formation of  $\text{AgCl}(s)$  is  $-26,187$  cal. at  $25^\circ$ . From the standard electrode potentials calculate the solubility product of  $\text{AgCl}$  and compare it with the experimental value of  $1.56 \times 10^{-10}$ .

15. Derive equation (11) from the relations

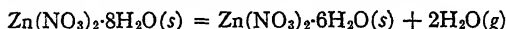
$$\frac{d \ln K}{dt} = \frac{\Delta H^\circ}{RT^2} \quad \text{and} \quad \Delta F^\circ = -RT \ln K$$

\* The difference between the answers of Problems 8 and 9 is due to experimental errors. The two would be the same if all the data were accurate.

16. The vapor pressure of a mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$  as a function of the temperature is given below. (a) Find graphically the heat of transition between these hydrated salts.

Temp.	34	30	25	20	15	10°
$p$	7.54	5.95	4.15	2.92	2.00	1.36 mm

(b) What is the free energy change at 25° in the reaction



(c) What is the entropy change in the reaction at 25°?

17. Calculate the activity of (a) acetone, and (b) ether in a solution in which ether has a mole fraction of 0.504.

(c) Calculate the free energy change involved when one mole of ether is evaporated from a very large quantity of solution in which the mole fraction of ether is 0.504 and condensed in a very large quantity of solution in which the mole fraction of ether is 0.066.

18. Calculate the activity of the solute in a 10 molal ideal solution where the molecular weight of the solute is 100 and where (a) the standard state of the solute is defined by letting  $a$  approach  $m$  as  $m$  approaches 0; (b) the standard state of the solute is defined by letting  $a$  approach  $N$  as  $N$  approaches 0.

19. The specific volumes at 25° for solutions of  $\text{KNO}_3$  are given in the accompanying table. Calculate the partial molal volumes of water and potassium nitrate in a 10 per cent solution.

Per cent by Weight	Specific Volume	Per cent by Weight	Specific Volume
0.000	1.00293	10.300	0.94096
5.361	0.97032	15.243	0.91207
9.963	0.94295	20.423	0.88227
10.132	0.94195	25.355	0.85429

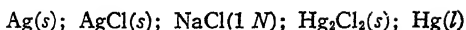
20. When 1 mole of water was added to an infinitely large amount of an aqueous methanol solution having a mole fraction methanol 0.40, the volume of the solution increased 17.35 ml. When 1 mole of methanol was added to such a solution, the volume increased 39.01 ml. Calculate the volume of a solution containing 0.40 mole of methanol and 0.60 mole of water.

21. Using a Debye function, calculations show the molal entropy of silver iodide to be 1.5 entropy units at 15° K. From the following data for the molar heat capacity of constant pressure, calculate the molal entropy of silver iodide at 298.1° K.

$T^\circ$	$C_p$	$T^\circ$	$C_p$	$T^\circ$	$C_p$	$T^\circ$	$C_p$
21.00	3.82	64.44	9.36	145.67	11.92	258.79	13.05
30.53	5.23	88.58	10.60	170.86	12.15	273.23	13.26
42.70	7.09	105.79	11.19	198.89	12.49	287.42	13.48
52.15	8.20	126.53	11.60	228.34	12.76	301.37	13.64

22. In the formation of 1 mole of  $\text{AgI}(s)$  from solid silver and solid iodine 14,815 cal. are evolved at 25°. From specific heat measurements at low temperatures the molal entropy of  $\text{AgI}(s)$  at 25° has been found to be 27.6 cal. per deg., whereas the atomic entropy of silver at 25° is 10.2 and that of iodine is 13.3 cal. per deg. Calculate the standard molal free energy of  $\text{AgI}(s)$  at 25°.

23. Calculate the electromotive force of the cell

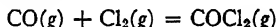


from the following standard free energies of formation

$\text{Ag}^+$	+18,488 cal./mole
$\text{AgCl}(s)$	-26,187
$\text{Na}^+$	-62,588
$\text{Cl}^-$	-31,367
$\text{Hg}_2\text{Cl}_2$	-50,274

24. In designing a thermal diffusion tower for the separation of the isotopes of carbon in methane it is necessary to know how high the heating unit can be raised in temperature without decomposing the methane. Approximately what is the highest temperature to which methane at atmospheric pressure can be heated without decomposing more than 1.0 per cent? Thermal data can be found in this chapter and in Chapter VI, or in Problems 3, 4, and 5.

25. The free energy of the reaction

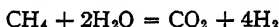


can be represented by the equation:

$$\Delta F^0 = -24,100 + 4T \ln T + 3.5T$$

Calculate the partial pressure of chlorine in equilibrium with phosgene at 200° and a total pressure of 1 atm., assuming that the gases are perfect gases.

26. At 377°,  $R \ln K = -16.44$  for the reaction



At 25° for this reaction  $\Delta H^0 = 39,432$ . Construct the equation showing the variation of  $\Delta F^0$  with temperature using specific heat data, and calculate the equilibrium constant at 500°.

27. The vapor pressure of a mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  is given as a function of temperature below. Find  $\Delta H^0$ ,  $\Delta F^0$ , and  $\Delta S^0$  at 25°.

Temp., °C.	39	38	37	35	30	25	20
$p$ , mm.	2.42	2.25	1.80	1.25	0.65	0.27	0.08

28. (a) Calculate the activities of the solvent ether and the solute acetone at a mole fraction of acetone of 0.2509 at 30°. (b) Calculate the value of  $\gamma$  in Table IV.

29. From the entropy values and the heats of formation given in Chapter VI, together with the value 29.1 cal. deg.<sup>-1</sup> mole<sup>-1</sup> for the entropy of  $\text{Ag}_2\text{O}$  at 25°, calculate  $\Delta F^0$  and  $K$  for the reaction



at 25°. What is the dissociation pressure of  $\text{Ag}_2\text{O}$  at 25°?

30. A solution 0.5 molar with respect to  $\text{H}_2\text{SO}_4$  and 1.5 molal with respect to zinc sulfate has a vapor pressure of 22.454 mm. at 25°. For the cell



$E = 0.69021$  volt and  $E^0$  is equal to 0.61515 volt. For the cell





$E = 1.44561$  volts and  $E^0 = 1.3765$  volts. The vapor pressure of pure water at  $25^\circ$  is 23.75 mm. (a) Calculate the activity of the water. (b) Calculate the mean activity of the sulfuric acid, and (c) the mean activity of the zinc sulfate.\*

31. Using the method of intercepts, calculate from the following data at  $3^\circ$  the partial molal heat capacities in calories per mole of water and ethanol for (a) a 15.0% ethanol solution, (b) a 44.0% ethanol solution.

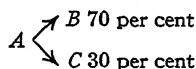
% Ethanol	Specific Heat (joule/gm.)	% Ethanol	Specific Heat
0.0	4.211	20.7	3.925
.02	4.316	28.1	3.622
4.16	4.379	37.0	3.367
6.46	4.395	47.7	3.132
8.91	4.362	61.0	2.802
11.5	4.282	77.9	2.568
14.4	4.186	100.0	2.263

32. Calculate graphically the entropy of  $\text{Na}_2\text{CO}_3$  at  $25^\circ$ , given the following data:

$T$	54.60	58.43	74.23	119.2	154.6	183.6	239.7	274.1°
$C_p$	6.878	7.579	10.53	16.96	19.88	21.56	24.43	25.81

Extrapolate the curve to  $0^\circ \text{K}$ . The correct value of  $S$  at  $54.60^\circ \text{K}$ . is 4.10 entropy units.

33. Given the following reaction at a certain temperature:



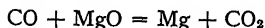
It is desired to make the reaction go in such a way as to produce a larger yield of  $B$ . What principles of thermodynamics and kinetics can be used in attacking this problem?

34. The following data for isobutene may be found in the literature. Using any that are necessary and looking up any further data that may be needed calculate the free energy of formation of gaseous isobutene at  $25^\circ$  (Todd and Parks, *J. Am. Chem. Soc.*, **58**, 134 [1936]).

$S_{298\text{K}} = 10.81$  entropy units  
 $\text{F.P.} = -140.7^\circ$   
 Heat of fusion = 25.22 cal./g.  
 $\text{B.P.} = -7.1^\circ$   
 Heat of vaporization = 96.5 cal./g.  
 $\Delta H$  of formation ( $25^\circ$ ) = -4060 cal.

	Specific Heat							
$T$	93.3	105.5	118.9	139.2	166.1	179.8	210.2	253.1°
$C$	0.2498	0.2749	0.3056	0.4547	0.4621	0.4681	0.4860	0.5173

35. Estimate roughly at what temperature carbon monoxide will reduce magnesium oxide according to the reaction



\* Tartar, Newschwander, and Ness, *J. Am. Chem. Soc.*, **63**, 28 (1941).

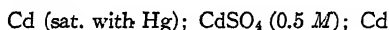
Magnesium boils at 1107°. According to thermodynamics, magnesium reacts chemically at temperatures of a few hundred degrees with oxygen, water, nitrogen, and carbon dioxide. Moreover, it reacts with carbon monoxide. Suggest possible ways in which metallic magnesium may be obtained from magnesia (MgO) and carbon. Suggest what difficulties may be encountered in the process.

36. Show that the free energy of mixing of two liquids which form a perfect solution is

$$-\Delta F = N_2 RT \ln N_2 + N_1 RT \ln N_1$$

37. From the data of Problems 8 and 9, show that there is a decrease of entropy in the sulfur system when monoclinic sulfur changes spontaneously into rhombic sulfur, but that there is an increase in the entropy of the surroundings which more than offsets this decrease. Thus the total entropy (of the universe) is increased, as required for a spontaneous reaction.

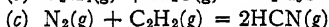
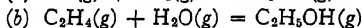
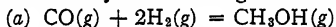
38. (a) Derive the formula for the entropy change accompanying a chemical reaction in terms of the temperature coefficients of the electromotive force of the corresponding electrical cell. (b) Calculate the free energy change and heat of reaction at 298° K. for the cell



where

$$E \times 10^5 = 5538 - 14.81T - 0.385T^2 + 0.0075T^3$$

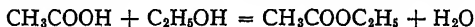
39. What are the possibilities of producing (a) methanol, (b) ethanol and (c) hydrocyanic acid by the following reactions:



Details of the thermodynamic calculations are given by Ewell in *Ind. Eng. Chem.*, **32**, 147 (1940).

40. Calculate the solubility of monoclinic sulfur in  $\text{CCl}_4$  at 25°. That of rhombic sulfur is 0.84 g. per 100 g. of  $\text{CCl}_4$ . Sulfur exists in both solutions at  $S_8$ . The free energy of formation of monoclinic sulfur is 18 cal. per mole greater than that of rhombic sulfur at 25°.

41. Compare the equilibrium constant in gas phase and in solution for the reaction



stating what differences, if any, exist.\*

42. The electromotive force of the cell



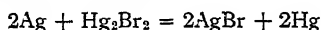
has been determined accurately by Dakin and Ewing (*J. Am. Chem. Soc.*, **58**, 984 [1936]), and the values of  $E^\circ_{\text{Ag, AgBr}}$  have been determined by Owen and Foering (*J. Am. Chem. Soc.*, **58**, 1575 [1936]). The data are as follows:

Temp.	$E_{\text{cell}}$	$E^\circ_{\text{Ag Ag Br (sat.)}}$
15	0.06492	0.07586
25	0.06804	0.07121
35	0.07116	0.06591

\* Essex, *J. Am. Chem. Soc.*, **54**, 1290 (1932).

(a) Calculate  $E^{\circ}_{\text{Hg}_2\text{Br}_2; \text{Hg}}$  at each temperature and find formulas which give  $E_{\text{cell}}$  and  $E_{\text{Hg}_2\text{Br}_2; \text{sat}}; \text{Hg}$  as a function of temperature.

(b) Calculate  $\Delta F^{\circ}$  at 25° for the reaction



(c) Calculate  $\Delta H$  for this reaction.

(d) Calculate  $\Delta S$  for this reaction.

(e) Using the free energy of formation of silver bromide  $\Delta F^{\circ} = -22,935$  cal. per mole, show that free energy of formation of mercurous bromide is  $-42,733$ .

43. Calculate the molal entropy of liquid chlorine at its melting point, 172.12° K., from the following data obtained by Giauque and Powell.

$T$ °K.	$C_p$ Cal. deg. <sup>-1</sup> mole <sup>-1</sup>
15	0.89
20	1.85
25	2.89
30	3.99
35	4.97
40	5.73
50	6.99
60	8.00
70	8.68
90	9.71
110	10.47
130	11.29
150	12.20
170	13.17
172.12	m.p.

Heat of fusion = 1531 cal. per mole.

A plot of  $C_p/T$  against  $T$  is most convenient for the graphical integration. Below 15° it may be assumed that  $C_p$  is proportional to  $T^3$ ,

## CHAPTER XIX

### QUANTUM THEORY

The quantum theory, first proposed by Planck in 1900, has had a profound influence on the development of science. Most of the recent researches in physics have been connected with quantum theory, and it is now being applied extensively in chemical investigations. The theory has led to advances in practical work no less important than those in theoretical work, and its findings have been so revolutionary as to lead to a new viewpoint in philosophy. There are two main themes in quantum theory — first that radiation is discontinuous, and second that there are restrictions imposed in the transfer of energy to molecules and electrons.

The quantitative description of these restrictions has been aided by the application of mathematical formulas, sometimes called wave equations. This newer extension of quantum theory is known as *quantum mechanics*.

The whole spectrum of radiant energy may be divided roughly as shown in the following scale.

TABLE I  
DIVISION OF THE SPECTRUM

Type of Radiation	Hertzian Waves	Infrared	Visible	Ultraviolet
Wavelength Ångströms Centimeters	$>10^{12} - 10^7$ $>10^8 - 10^{-1}$	$10^7 - 8000$ $10^{-1} - 8 \times 10^{-5}$	$8000 - 4000$ $8 \times 10^{-5} - 4 \times 10^{-5}$	$4000 - 500$ $4 \times 10^{-5} - 5 \times 10^{-8}$

Type of Radiation	X Rays	Gamma Rays	Cosmic Radiations
Wavelength Ångströms Centimeters	$500 - 1$ $5 \times 10^{-8} - 1 \times 10^{-9}$	$1 - 0.1$ $1 \times 10^{-8} - 1 \times 10^{-9}$	$<0.0001$ $<1 \times 10^{-12}$

The Hertzian or radio waves are generated by electrons oscillating along a wire, and they are absorbed by an antenna wire having the proper capacity and inductance. Infrared or heat rays are generated and absorbed by the rotation of molecules and by the displacement of atoms in molecules. Visible and ultraviolet radiations are absorbed

when outer electrons are displaced in molecules and atoms, and are evolved when the electrons return toward their normal positions. The displacements and the energy requirements are greater in ultra-violet light. X rays involve the displacement of inner electrons in atoms; gamma rays involve the displacements of particles still deeper, in the nucleus of the atoms. Cosmic rays, in so far as they consist of radiations, have very short wavelengths and are exceedingly penetrating. They appear to be generated in interstellar space.

**Emission and Absorption.** When light strikes a substance, a portion of the incident radiation is transmitted, a portion is reflected, and a portion is absorbed. These three possibilities are illustrated by the passage of visible light through glass, the reflection from silvered glass, and the absorption by smoked glass.

It has been established by Kirchhoff that the ability of a given substance to emit radiation when heated is proportional to its ability to absorb radiation. Denoting the emission and absorption by  $E$  and  $A$  respectively,

$$E = sA \quad [1]$$

where  $s$  is constant.

When absorption is complete,  $A$  is unity and  $E = s$ . Under these conditions the constant  $s$  may be defined as the emissivity of a body which absorbs all the incident radiation and reflects none. Such a body is called a *black body* or *perfect radiator*. A hollow, blackened sphere perforated by a small hole to permit the passage of the radiation is a close approximation to a perfect radiator. Practically all the radiation passing into the small opening is absorbed by multiple reflections at the inner surface. Likewise, when the sphere is heated the radiation emitted has the maximum intensity that it can have at a given temperature. An electrically heated furnace with a small opening, or even a heated blackened strip of platinum, serves as a convenient but imperfect substitute for a perfect radiator.

The value of the emissivity constant,  $s$ , is the same for all materials at a given temperature, but the emission  $E$  decreases when the absorption becomes less than 100 per cent, as shown by equation (1).

It can be shown that the law of Kirchhoff is a necessary consequence of the application of the second law of thermodynamics to the thermal equilibrium within an enclosure the walls of which are impervious to heat.

Kirchhoff's law may be readily illustrated with a fragment of white chinaware, decorated with a dark pattern, and heated to a high temperature. When the fragment is cold, the dark parts absorb

light, whereas the white parts reflect it. When the fragment is heated to redness, the pattern is reversed, the dark portions of the design appearing bright, and the white portions dark. When it is placed inside a heated furnace with a small opening, the design disappears.

**Laws of Radiation.** From a study of the experiments of Dulong and Petit on the rate of cooling of different bodies, Stefan discovered in 1879 an empirical relation between the total radiation of a body and its temperature. Later, Boltzmann derived the same relation thermodynamically and showed that instead of being general, as Stefan supposed, it is strictly applicable only to a perfectly black body. The Stefan-Boltzmann law may be stated as follows: *The total radiation from a perfect radiator is directly proportional to the fourth power of the absolute temperature.* If the total radiation is denoted by  $E$ , we may write

$$E = \sigma T^4 \quad [2]$$

where  $\sigma$  is a constant. This law is tested by measuring the heat radiated from the small opening in a heated vessel and received on a thermopile. From measurements of the quantity of radiation striking the receiver per second at various temperatures,  $\sigma$  has been found to have the value  $5.69 \times 10^{-5} \text{ erg cm.}^{-2} \text{ sec.}^{-1} \text{ deg.}^{-4}$

*Example 1.* An electrical furnace heated to  $727^\circ$  has a small hole 2 sq. cm. in area which is pointed at a wall. How many calories of heat hit the wall in an hour?

$$E = 5.69 \times 10^{-5} \times 2 \times 3600 \times (1000)^4 / 4.183 \times 10^7 = 9790 \text{ cal.}$$

If the radiation from the sun is considered solely as a temperature effect, its temperature may be calculated by equation (2) expressing the Stefan-Boltzmann law. Employing available data, the temperature of the sun is estimated to be  $6200^\circ \text{ K.}$

The total energy radiated by a given source having been considered, the distribution of energy throughout the entire spectrum will now be discussed, particularly with respect to the temperature. The distribution of energy in the normal spectrum of a black body is represented graphically in **Fig. 138**. The energy radiated by the source in arbitrary units is plotted against the corresponding wavelengths in microns ( $1 \mu = 10^{-4} \text{ cm.} = 10,000 \text{ \AA.}$ ).

These measurements may be made by spreading out with a suitable prism the total radiation from a perfect radiator. A thermopile is then moved along in different parts of the spectrum, and the deflections of the galvanometer connected to the thermopile are proportional to the intensity of radiation falling on the receiver.

It will be observed that the energy corresponding to a definite wavelength increases with the temperature, and that each curve, or isothermal, exhibits a distinct maximum. The position of this maximum is

displaced in the direction of decreasing wavelength as the temperature is raised.

This displacement of the energy maximum with temperature is given by Wien's law. Wien showed that, if  $\lambda_{\text{max}}$  denotes the wave length corresponding to the energy maximum, and  $T$  is the absolute temperature of the radiating black body

$$\lambda_{\text{max}} \times T = \text{Constant} \quad [3]$$

Furthermore, Wien found that

$$E_{\lambda \text{ max.}} = BT^5 \quad [4]$$

where  $E_{\lambda \text{ max.}}$  is the maximum emission corresponding to  $\lambda_{\text{max}}$ . In general, the emissivity  $E_{\lambda}$  is the amount of energy radiated per square centimeter per second in a narrow strip of the spectrum corresponding to the mean wavelength  $\lambda$ .

The actual distribution of energy throughout the spectrum resolves itself

into the measurement of the energy emitted between two contiguous wavelengths,  $\lambda$  and  $\lambda + d\lambda$ . In other words, actually the energy of a very small portion of the spectrum included between two wavelengths, which lie very close together, is measured. Formulas of Rayleigh and Wien have been found to reproduce the experimental values with considerable accuracy in limited regions. The distribution formula of Rayleigh has the following form

$$E_{\lambda} = \frac{C_1}{\lambda^5} (\lambda T) \quad [5]$$

while that of Wien may be written thus

$$E_{\lambda} = \frac{C_2}{\lambda^5} \cdot e^{-C_3/\lambda T} \quad [6]$$

In these formulas,  $C_1$ ,  $C_2$ , and  $C_3$  are constants, and the other symbols have their usual significance. The formula of Rayleigh holds only in the region of the longer wavelengths, whereas the formula of Wien

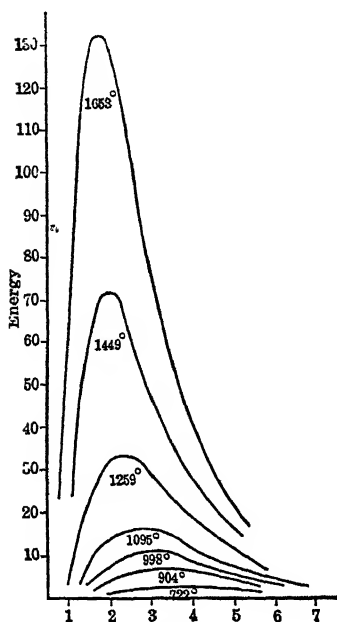


FIG. 138

holds only for short waves. It should be remembered that both these formulas apply only to bodies emitting continuous spectra.

**Origin of Quantum Theory.** Realizing the limitations of these formulas, Planck derived a better equation which expressed the experimental facts with remarkable exactness over the whole range of the spectrum. In deriving this equation Planck was led to the arbitrary conclusion that radiation is emitted and absorbed discontinuously in integral multiples of a fundamental unit which he called a quantum  $\epsilon$ , and that the energy of a quantum is proportional to the frequency of the light. These suggestions led to the *quantum theory*.

The development of the quantum theory is one of the important milestones in the progress of science. As in many other important advances, the exact experimental facts came first, then an empirical mathematical equation to express the facts, and, finally, a working hypothesis to explain the terms in the equation. Then, on the basis of this hypothesis, predictions were made and new experiments planned which led to rapid progress in many different fields of science. General confirmation of the hypothesis soon gave it the rank of a theory.

Planck's formula\* is

$$E_{\lambda} = \frac{2\pi c^2 h}{\lambda^5 (e^{ch/k\lambda T} - 1)} \quad [7]$$

where  $E_{\lambda}$  is the rate of emission of radiation of wavelength  $\lambda$ ,  $c$  is the velocity of light,  $k$  is the gas constant per molecule ( $R/N$ ) called the Boltzmann constant, and  $h$  is a constant now known as Planck's constant. This proportionality constant  $h$  has turned out to be a very important universal constant.

Formula (7) can be integrated to give the Stefan-Boltzmann law; it approaches the Rayleigh law as  $\nu$  approaches zero, and it approaches the Wien distribution law as  $\nu$  approaches infinity. Moreover, it is in agreement with the Wien displacement law. Planck's radiation formula then is in remarkable agreement with the various facts of radiation, and it gives experimental values with excellent precision. In spite of these successes the formula would probably have failed to obtain general acceptance on account of the radically new assumption concerning quanta, except for the fact that almost at once it became extremely useful in new and unrelated fields. It has revolutionized the study of spectroscopy. Critical potentials, photoelectric effects, and specific heats have all been interpreted quantitatively with the help of the quantum theory. The study of photochemistry and chemi-

\* This formula is discussed fully in Taylor and Glasstone, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1942, pp. 189-196.



cal kinetics and the calculation of equilibrium constants (page 653) have been stimulated by applications of quantum mechanics.

According to the classical theories of specific heats there is an *equipartition of energy* among the different atoms in a molecule. The molar heat capacity at constant volume is  $\frac{3}{2}R$  (page 104) for monatomic gases, and there are three possible directions and three degrees of freedom in the translational energy. Each degree of freedom then has associated with it  $\frac{1}{2} \times \frac{3}{2}R = 1$  cal. per degree. For each extra atom in the molecule there are more degrees of freedom and a greater heat capacity. Actually, however, the polyatomic gases have heat capacities which are much less than those calculated on the basis of the number of degrees of freedom. Also, there is nothing in the classical theory to lead one to expect the large temperature coefficient of heat capacity which is actually found. Furthermore, diatomic hydrogen gas at temperatures below 70° K. has a molar heat capacity of 3 cal. and behaves exactly as a monatomic gas. Again, on the classical theory, crystals of solid elements should have a heat capacity of 5.9 calories per degree (page 108), but a few crystals like carbon, and in fact all crystals at sufficiently low temperatures, have a heat capacity much smaller than 5.9. Apparently some of the degrees of freedom are "frozen up" at the lower temperatures. The restricting of the degrees of freedom found an explanation in the quantum theory of restricted energy units, and formulas involving the quantum,  $h\nu$ , were applied, with considerable success, to specific heats at low temperatures.

There seems, then, to be adequate experimental justification in many fields for the quantum theory, according to which radiation is composed of units called quanta, and the energy of each quantum  $\epsilon$  is given by the equation

$$\epsilon = h\nu \quad [8]$$

where  $h$  has the value  $6.624 \times 10^{-27}$  erg-second and  $\nu$  is the frequency of the radiation in reciprocal seconds. In many applications of the theory, quantum numbers appear as integers in the various formulas, as indicated later.

**Spectroscopy.** The quantum theory has had its greatest success in the interpretation of spectra, and the pioneer work is due to Bohr\* who, in 1913, proposed the fundamental hypothesis that electrons exist in definite energy levels,  $E_1$ ,  $E_2$ , etc., without emitting or absorbing radiation, but that, when an electron changes from one level to another, monochromatic radiation is emitted or absorbed in accord-

\* Bohr. *Phil. Mag.*, **26**, 1, 476, 857 (1913).

ance with the following equation

$$E_2 - E_1 = \epsilon = h\nu \quad [9]$$

Bohr assumed that the electrons revolve around the nucleus in elliptical orbits, and that the centrifugal force is equal to the force of electrostatic attraction. In accordance with the new ideas he assumed further that the motion of the electron was *quantized*, and that instead of an infinite number of possible orbits there is only a restricted number with properties represented by functions of the quantum number  $n$ , where  $n$  is an integer 1, 2, 3, 4,  $\dots$ . By a simple application of mechanics and electrodynamics, given in the appendix on page 670, he showed that the energy  $E_n$  in a particular orbit  $n$  is

$$E_n = \frac{-m(Ze)^2 e^2 4\pi^2}{2n^2 h^2} \quad [10]$$

where  $m$  is the mass of the electron,  $Z$  is the atomic number (page 626),  $e$  is the charge on the electron,  $h$  is Planck's constant, and  $n$  is an integer. Then according to equation (8) the quantum of light emitted on changing from one orbit to another is given by the formula

$$\epsilon = h\nu = E_{n_2} - E_{n_1} = \frac{2\pi^2 m e^4 Z^2}{h^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad [11]$$

Several of these quantities can be grouped together giving a constant known as the Rydberg constant  $R$ , defined as follows:

$$R = \frac{2\pi^2 m e^4}{h^3 c} \quad [12]$$

in which  $c$  is the velocity of light.

Then substituting into equation (11), for hydrogen with an atomic number of 1

$$\tilde{\nu} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad [13]$$

where  $R_H$  has the value  $109,677.58 \text{ cm}^{-1}$  and  $\tilde{\nu}$  refers to wave numbers.

The different ways of expressing radiation are reviewed in the following equations:

$\lambda$  = wavelength.  $1 \text{ \AA.} = 0.0001 \mu = 10^{-7} \text{ mm.} = 10^{-3} \text{ cm.}$

$c$  = velocity of light  $= \lambda\nu = 3 \times 10^{10} \text{ cm. per sec. (approximately).}$

$\nu$  = frequency  $= \frac{3 \times 10^{10}}{\lambda_{\text{cm.}}}$

$\tilde{\nu}$  = wave number  $= \frac{1}{\lambda_{\text{cm.}}} \text{ (measured in } \textit{vacuo}.)$

$\nu = (3 \times 10^{10}) \tilde{\nu}.$

*Example 2.* Express green light of  $5000 \text{ \AA}$  in terms of centimeters, frequency, and wave numbers.

$$5000 \text{ \AA} = 5000 \times 10^{-8} = 5 \times 10^{-5} \text{ cm.}$$

$$\nu = \frac{3 \times 10^{10}}{5 \times 10^{-5}} = 6.0 \times 10^{14}$$

$$\tilde{\nu} = \frac{1}{5 \times 10^{-5}} = 20,000$$

Now the visible lines in the spectrum of hydrogen had been measured accurately, and Balmer, in 1885, pointed out that they could be represented by an empirical formula equivalent to the following

$$\tilde{\nu} = A \left( \frac{1}{2^2} - \frac{1}{n_2^2} \right) \quad [14]$$

where  $n_2$  is a whole number greater than 2 and  $A$  is a constant. It is obvious that equation (13) is the same as equation (14) and that it constitutes an excellent check on the theoretical calculations. In fact, the numerical value of  $R$ , expressed in eight significant figures, was obtained from exact spectral measurements rather than from equation (12), because some of the constants in equation (12) are known only to one part in a thousand.

It will be noticed in equation (14) that  $n_2$  cannot be less than 2 for then  $\tilde{\nu}$  would be a meaningless negative number, and that it cannot be 2 for then  $\tilde{\nu}$  becomes zero. As  $n_2$  becomes larger than 2 the corresponding value of  $\tilde{\nu}$  becomes larger, but when  $n_2$  is already large further increases cause  $\tilde{\nu}$  to increase only very slightly, and as  $n_2$  approaches infinity  $\tilde{\nu}$  approaches  $\frac{1}{4}R_H$ .

A few of the lines of the Balmer series as calculated by equation (13) setting  $n_1 = 2$  are given in Table II.

The success of the Balmer formula led to further exploration, and Lyman found another series in the ultraviolet spectrum of hydrogen which is just as satisfactorily represented by formula (13), provided  $n_1$  is given the value 1. Then  $n_2$  has values 2, 3, 4, etc. The lines calculated from this formula are known as the Lyman series. The Paschen series occurs in the infrared, and these lines are accurately reproduced by formula (13) when  $n_1 = 3$  and  $n_2$  has values greater than 3. These series are represented diagrammatically in Fig. 139. Light is emitted when the electron returns from a level of high energy (large quantum number) to a level of lower energy.

The intimate connection between these energy levels and the actual lines in the spectrum may be seen by comparing the energy levels plotted logarithmically, in Fig. 139, with the spectral lines in Fig. 140,

TABLE II  
BALMER LINES IN THE HYDROGEN SPECTRUM

$n_2$	$\tilde{\nu}_{\text{calcd.}} \text{ (vacuo)}$	$\lambda, \text{\AA}_{\text{calcd.}}^* \text{ (vacuo)}$	$\lambda, \text{\AA}_{\text{obsd.}}^* \text{ (air)}$
3	15,233.02	6,564.75	6,562.8
4	20,564.57	4,862.73	4,861.4
5	23,032.33	4,341.72	4,340.5
6	24,372.83	4,102.90	4,101.8
10	$x$	$y$	.....

\* Wavelengths are measured in air. Wave numbers,  $\tilde{\nu}$ , are the reciprocals of the wavelengths measured in vacuo.

$$\tilde{\nu} = \frac{1}{\lambda_{\text{vacuo}}} = \frac{n_{\text{air}}}{\lambda_{\text{air}}}$$

where  $n$  is the refractive index of air. Correction terms  $\lambda_{\text{air}}$  to  $\lambda_{\text{vacuo}}$  are given at different wavelengths in the International Critical Tables Vol. 7, page 5, McGraw-Hill Book Co., New York, 1930.

which are adapted from an ultraviolet spectrogram of a star by R. H. Curtiss. The same séquence of lines is observed, converging to a

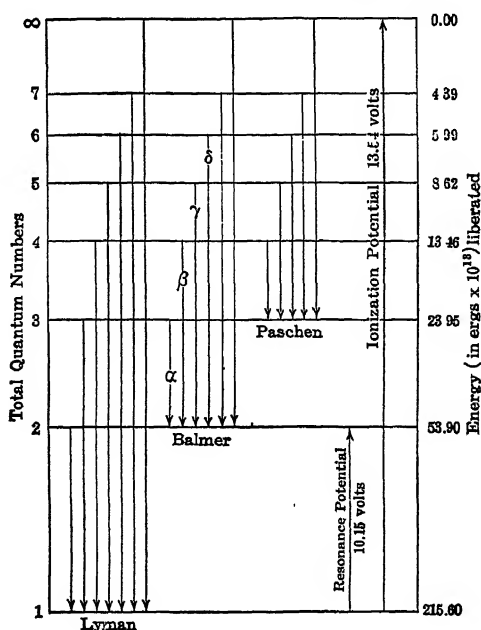


FIG. 139

limit. A much larger number of lines (35) has been observed in certain stars than in laboratory experiments because the gas pressures are low and there is more room for the large "orbits."

The continuous emission beyond the convergence limit of the lines shown in Fig. 140 is always present, and it is particularly significant.

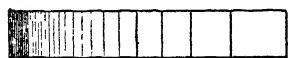


FIG. 140

In the region where sharp lines are obtained definite quantum restrictions are involved, but when the electron comes in from an indefinitely great distance the electron can bring with it unquantized kinetic energy which can vary continuously in magnitude and thus it can give a continuous range of frequencies. The convergence limit in the spectral series corresponds then to complete separation of the electron, i.e., to ionization.

In this discussion the emission of light has been emphasized, but the absorption mechanism is the same except that the electrons are driven out to levels of higher energy by the absorption of quanta of energy, whereas in emission they fall back to levels of lower energy.

Similar formulas have been developed for helium and the alkali metals and other elements involving a single valence electron. Each element has a slightly different value of the Rydberg constant  $R$ . For helium it is 109,722.26. For the elements heavier than hydrogen and helium it is necessary to apply correcting terms, which become smaller as the quantum numbers  $n_2$  become larger.

Bohr's formula was so successful in calculating the lines of the hydrogen spectrum with exactness that the model on which it was based was generally accepted. The elliptical orbits seemed perfectly natural by analogy with the orbits of the planets, but of course it does not follow that because a mechanism gives results which agree with experimental facts the mechanism is proved. Still other mechanisms may give the same results. In this particular case the quantum numbers are important but they do not necessarily come from elliptical orbits. In fact, a more complicated mathematical model based on wave mechanics has now been devised which works just as well in predicting the positions of the lines, and, in addition, it gives the intensities of the lines and it applies also to the elements heavier than hydrogen. The elliptical orbits then are not to be taken literally.

**Quantum Numbers.** The spectrum of atomic hydrogen can be interpreted nicely by the simple Bohr formula making use of two numbers. Other spectra are much more complicated, and more quantum numbers are needed in calculating the spectral lines. It is found that many spectral lines have fine structure. With sufficient dispersion they are seen to give doublets, triplets, etc. Furthermore, some of the lines are affected by a strong electrostatic field giving the *Stark effect* and by a magnetic field giving the *Zeeman effect*. In the

more complex spectra some of the lines can be grouped together in overlapping series depending on their behavior and on their general appearance. Thus, one series of lines is characterized by having particularly sharp lines and another by having diffuse lines. The diffuseness is due to the fact that more lines are possible on account of a greater variety of energy levels, and the many lines are not separated except with a spectroscop of high resolution. Several characteristic types of spectra have come to be recognized by spectroscopists, such as the principal (*p*), sharp (*s*), diffuse (*d*), fundamental (*f*).

Now all these variations can be handled by using four quantum numbers. These numbers and their symbols which describe the state of an electron in an atom are as follows:

$n$  = principal quantum number (or total quantum number).

When $n =$	1	2	3	4	5
the corresponding symbols are	$K$	$L$	$M$	$N$	$O$ .*

$l$  = orbital quantum number.

$l$  can have any integer value, except that it must be one or more units less than the principal quantum number, i.e., it can never be greater than  $(n - 1)$ .

When  $l =$                       0   1   2   3

the corresponding symbols are  $s$   $p$   $d$   $f$

$m_l$  = magnetic quantum number.

$m_l$  depends on  $l$  and may have any integral value between  $+l$  and  $-l$ , including zero. Therefore,  $2l + 1$  values of  $m_l$  are possible.

$m_s$  = electron spin number.

Two values of  $m_s$  are possible, corresponding to two possible orientations of the spin vector  $s^\dagger$ . The quantum numbers can vary only by integers, and  $m_s$  can have only the values  $+\frac{1}{2}$  and  $-\frac{1}{2}$ .

Definite physical concepts, such as the spinning of the electron, were originally attributed to these different quantum numbers, but it is neither necessary nor profitable to attach definite mechanical or electrical significance to them. They may be considered merely as arbitrary numbers which serve to describe physical and chemical facts when they are substituted into mathematical formulas.

Only those combinations of numbers are allowed which are in agrée-

\* These letters refer to the shells of the outer electrons as described on page 638 *K* referring to the first electron shell outside the nucleus, *L* to the second, *M* to the third, etc.

† The spin quantum number  $s$  is not the same as the orbital quantum number  $s$ .

ment with the restrictions just given. For example, if  $n = 3$ ,  $l$  can be only 2, 1, or 0; and  $m_l$  can be  $\pm 2$ ,  $\pm 1$ , or 0; and  $m_s$  can be only  $+\frac{1}{2}$  or  $-\frac{1}{2}$ .

All the various combinations of the four quantum numbers, permitted by the restrictions just given, are recorded in Table III.

TABLE III  
POSSIBLE CONDITIONS OF ELECTRONIC QUANTUM NUMBERS

Principal $n$	Group	Orbital $l$	Sub- group	Magnetic $m_l$	Spin $m_s$	Total Number of Different Combina- tions
1	(K)	0	(s)	0	$+\frac{1}{2} - \frac{1}{2}$	2
2	(L)	0	(s)	0	$+\frac{1}{2} - \frac{1}{2}$	2
2	(L)	1	(p)	+1 0 -1	$+\frac{1}{2} - \frac{1}{2}$	6
3	(M)	0	(s)	0	$+\frac{1}{2} - \frac{1}{2}$	2
3	(M)	1	(p)	+1 0 -1	$+\frac{1}{2} - \frac{1}{2}$	6
3	(M)	2	(d)	+2 +1 0 -1 -2	$+\frac{1}{2} - \frac{1}{2}$	10
4	(N)	0	(s)	0	$+\frac{1}{2} - \frac{1}{2}$	2
4	(N)	1	(p)	+1 0 -1	$+\frac{1}{2} - \frac{1}{2}$	6
4	(N)	2	(d)	+2 +1 0 -1 -2	$+\frac{1}{2} - \frac{1}{2}$	10
4	(N)	3	(f)	+3 +2 +1 0 -1 -2 -3	$+\frac{1}{2} - \frac{1}{2}$	14

The total number of permissible combinations of the four quantum numbers is given in the last column of Table III. The recognition of these four quantum numbers has been a great aid in understanding many physical and chemical phenomena particularly through the application of the restriction to be described in the following section.

The further application of these quantum numbers to describe complicated spectra is beyond the scope of this book. It may be stated, however, that the capital letters  $S$ ,  $P$ ,  $D$ , and  $F$  are used to designate atomic states rather than the states of individual electrons, and that superscripts before a letter refer to the number of sublevels in the state, giving doublets, triplets, etc. Spectral lines are described in terms of the difference between two atomic energy states, each designated by quantum numbers.

**Pauli's Exclusion Principle.** According to Pauli, *two electrons in a single atom can never have all four quantum numbers the same*. This principle is a great help in explaining the spectral lines, and the number of elements in the different groups of the periodic table. Referring

to the last column in Table III, it is seen that two different combinations of quantum numbers are possible for an  $s$  electron, six for a  $p$  electron, 10 for a  $d$  electron, etc. Now, by the Pauli principle, there can be only one kind of atom for each given combination of electronic quantum numbers. The different atoms have different combinations of quantum states. The sequence 2, 8, 18, 32 given in the last column of Table III is related to the sequence in the number of elements found in the successive groups of the periodic table as shown later on page 639.

**Critical Potentials.** When free electrons are passed through a gas at a low pressure they must have certain velocities in order to be stopped just as light must have certain frequencies in order to be absorbed by a given material. The energies of the electrons must be sufficient to correspond to definite energy transitions in the molecule or there can be no interaction. This is a fundamental postulate of the quantum theory.

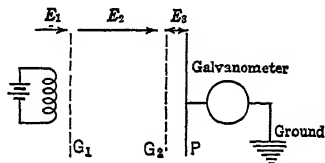


FIG. 141

The apparatus shown in Fig. 141 is a simple one which permits the direct experimental measurement of critical potentials. A filament is heated to emit electrons, and an adjustable potential  $E_1$  of several volts is applied between it and the grid  $G_1$ , the latter being charged positively. When the tube is thoroughly evacuated the electrons coming from the filament are driven through the grid and across the tube to the plate  $P$ , whence they pass through the galvanometer to the ground. An opposing potential  $E_3$  is increased until the electrons are barely able to reach the plate. A trace of gas, mercury vapor for example, is next admitted, and the slow-moving electrons suffer many elastic collisions with the molecules without loss of energy and they still reach the plate and are registered by the galvanometer. As the potential  $E_1$  is increased gradually, the current through the galvanometer increases. Eventually, however, the current decreases suddenly because the electrons have acquired sufficient kinetic energy to cause a definite displacement of electrons from one energy level to a higher energy level, in the molecules composing the gas. This effect is due to inelastic collisions in which the energy of the moving electron is consumed by the molecule, and after these collisions the electrons do not retain sufficient velocity to reach the plate. As the potential is increased still further, the electrons acquire more energy, some of which is retained after collision. The subsequent collisions of these electrons with other molecules again become elastic and the electrons reach



the plate and register an increased current through the galvanometer.

This process is continued as the potential is gradually increased until the electrons acquire kinetic energy sufficient to produce another dis-

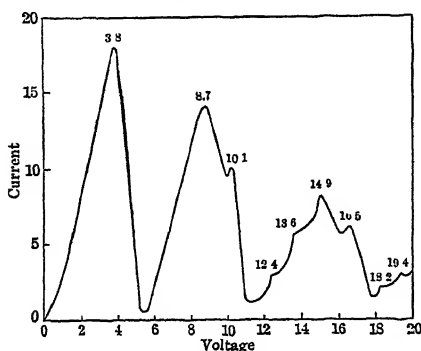


FIG. 142

placement of the electron in the atom. Then the collisions become inelastic and the current drops abruptly as before. Several peaks corresponding to definite energy changes are recorded. A curve of this type, in which electron current is plotted against the voltage, is shown in Fig. 142, where Einsporn's data\* on mercury vapor are given. The critical potentials are taken as the voltages at which the current

first starts to decrease, but it is necessary to apply a correction to all the values shown in Fig. 142 because the electrons leave the filament with a definite kinetic energy, in this case amounting to 1.1 volts. The first critical potential then is 4.9 rather than 3.8.

The second grid  $G_2$  and reversible potentials  $E_2$  and  $E_3$  are designed to distinguish between the two kinds of critical potentials, namely, ionization potentials and resonance potentials.

An *ionization potential* is the voltage which gives to a free electron just sufficient energy to ionize the atom or molecule, i.e., to drive an electron completely out, leaving a positive ion but without imparting any kinetic energy to the electron. *Resonance potentials* are potentials sufficiently great to cause the emission of light when the free electrons are stopped by collision. They involve the displacement of valence electrons to higher energy levels and their return to lower energy levels with the emission of light in accordance with equation (9).

An obvious and simple relation between the electrical energy, the kinetic energy, and the radiation energy is involved in these quantum changes, as given by the following equation

$$E'e = \frac{1}{2}mv^2 = h\nu \quad [15]$$

where  $e$  is the charge on the electron in electrostatic units ( $4.80 \times 10^{-10}$ ),  $m$  its mass, and  $v$  its velocity, and  $E'$  is the potential drop in electrostatic volts through which the electron falls. All the quantities must be expressed in the same c.g.s. units. Since by definition one ordinary

\* Einsporn, *Z. Physik*, 5, 208 (1921).

or international volt is equal to  $1/300$  electrostatic volt  $E/300 = E'$ , and

$$\frac{E}{300} e = h\nu \quad [16]$$

It is convenient to remember that the energy of a quantum expressed in electron-volts  $E$  is 12,395 divided by the wavelength in angstroms.

Referring to page 555

$$\frac{Ee}{300} = h\nu = hc\tilde{\nu} = hcR\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad [17]$$

or

$$E = \frac{300Rhc}{e}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad [18]$$

where  $n_1$  and  $n_2$  are the quantum numbers 1, 2, 3, 4, 5, etc.

This equation is used in Table IV to show the numerical relation between spectral lines and critical potentials in the Lyman series of *atomic* hydrogen, where  $n_1 = 1$ . The constant  $300Rhc/e$  has the value of 13.539.

TABLE IV  
COMPARISON OF SPECTRAL LINES AND CRITICAL POTENTIALS

Quantum Number $n_2$	Wavelength $\tilde{\lambda}_{\text{obsd.}}$	Wave Number $\text{cm}^{-1}$	Volts $E_{\text{calcd}}$	Volts $E_{\text{obsd.}}$
2	1215	82,258	10.154	10.15
3	1026	97,491	12.034	12.05
4	973	102,823	12.692	12.70
5	950	105,291	$\infty$	.....
6	938	106,631	13.161	13.17
7	931	107,440	13.262	13.27
$\infty$	912	109,678	13.539	13.54

The agreement between the calculated and observed voltages is excellent, again strengthening the underlying quantum theory on which the calculations are based. In many cases it is possible to show the actual emission of light of the expected frequency by bombarding with electrons of the proper voltage, new spectral lines being brought in as the voltage is increased.

Electron velocities and even spectral quantities are often expressed in terms of volts, calculated with the help of equation (18). The term volt when applied to energy quantities really means electron-volt. The relation between electron-volts, wave numbers, frequencies,

angstrom units, and kilogram calories per mole is given graphically on page 581.

A beam of electrons has many of the properties of a beam of light of extremely short wavelengths. Use has been made of this fact in determining the structure of molecules (page 237) and in taking photomicrographs of objects too small to be rendered visible with a microscope and ordinary light.

**The Photoelectric Effect.** Light quanta can be emitted by bombardment with electrons as just shown, and it is to be expected that electrons can be emitted by bombardment with quanta of light. In 1887, Hertz discovered that, when a spark gap is exposed to ultraviolet radiation, the voltage necessary for the passage of a spark is appreciably lowered. This effect is due to the emission of electrons, and the consequent ionization of the air between the terminals of the spark gap. A sheet of zinc acquires a positive charge when illuminated with ultraviolet light, owing to the emission of electrons. The ejection of electrons from a metal surface by means of light is known as the photoelectric effect.

This interesting effect has been utilized in the photoelectric cell, which is an extremely sensitive instrument for the detection and measurement

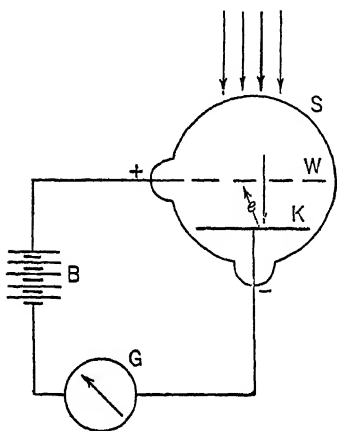


FIG. 143

of radiation. A diagram of such a cell is shown in Fig. 143.

A receiver  $K$  is coated with a thin film of potassium or other metal in a highly evacuated tube. A wire,  $W$ , placed in the tube is connected with the receiver through a 100-volt battery  $B$  and a sensitive galvanometer or electrometer  $G$ . The high vacuum of the tube serves as a complete insulator between  $W$  and  $K$ , but, when the receiver is exposed to light from the source  $S$ , electrons are ejected from the receiver and attracted to the positively charged wire, thus completing the circuit. The current registered by the galvanometer is directly proportional to the number of electrons released per second, and this in turn is proportional to the number of photons striking the receiver, i.e., to the intensity of the light.

Although the electron current or the number of electrons per second depends on the intensity of light, i.e., on the number of photons (quanta) striking the surface per second, the velocity or energy of

the ejected electrons, depends on the frequency of the light, according to the quantum relation

$$\frac{1}{2}mv^2 = E'e = h\nu - h\nu_0 \quad [19]$$

where  $m$  and  $v$  denote the mass and velocity of the electrons, respectively.  $E'$  is the potential difference in electrostatic units necessary to retard the velocity of the electron to zero;  $e$ , the electronic charge in electrostatic units;  $\nu$ , the frequency of the incident radiation;  $\nu_0$ , the limiting frequency (sometimes termed the "photoelectric threshold"); and  $h$ , Planck's constant. In equation (19),  $h\nu$  measures the energy absorbed by the electron from the incident radiation;  $h\nu_0$  represents the energy consumed in bringing the electron to the surface of the metal; and  $\frac{1}{2}mv^2$  is the actual kinetic energy of the emergent electron. This latter magnitude is measured by the product  $E'e$ .

When the maximum voltage  $E$  required to prevent the production of an electron current is plotted against the frequency  $\nu$  of the incident light a straight line is obtained having a slope equal to  $h/e$ . This relation has been accurately checked with many different metals. The experimental determination of the slope offers one means of evaluating Planck's constant  $h$  (in terms of  $e$ ).

The current in a photoelectric cell can be amplified readily, with the aid of ordinary electron tubes, to operate a relay, and the photoelectric cell is finding many important applications in automatic controls, safety devices, and laboratory appliances, as well as in television and motion pictures.

**The Compton Effect.** The photoelectric effect involves the complete absorption of a quantum, but it is possible also for a quantum to impart only a portion of its energy to an electron. This phenomenon in which the energy of the photon is reduced and the energy of the electron is increased is known as the *Compton effect*. The photon of light collides with an electron and leaves with a lower frequency, and the electron acquires a greater velocity. Compton\* bombarded carbon and other light elements with short x rays and found, with the help of a crystal lattice and spectrometer, that part of the scattered radiation had a longer wavelength than the incident radiation.

This fundamental experiment, together with the realization that any physical measurement involves interaction with the measuring instruments, led Heisenberg† through mathematical considerations to the *principle of uncertainty*. According to this principle it will never be possible to know with exactness *both* the position and the momentum

\* Compton, *Phys. Rev.*, **21**, 483 (1923).

† Heisenberg, *Z. Physik*, **43**, 172 (1927).

of an electron or other small particle. It is not a matter of physical imperfections in the measuring apparatus but a fundamental limit of nature, according to which the error in measuring position multiplied by the error in measuring momentum is approximately of the order of Planck's constant  $h$ . The position of an electron or atom may be known with exactness, but then its velocity is unknown; and in the same way the momentum can be known only at the sacrifice of, information regarding the position.

The principle is of no importance in ordinary work because the particles involved are so large that the uncertainty is utterly negligible. It does have an important bearing on philosophy,\* however, for heretofore it had been supposed that no *theoretical* limit was imposed on the precision of scientific measurements.

**The Raman Effect.** A photon of radiation may undergo elastic collision with a molecule, in which case the scattered light has the same frequency as the incident light. It may be absorbed completely in producing heat or chemical reaction; or it may contribute part of its energy to displacements of the atoms within the molecule. These atomic displacements are quantized, i.e., only certain displacements are possible, corresponding to definite energy increments. Each of these quantized atomic displacements gives rise to absorption in the infrared portion of the spectrum.

The *Raman effect* involves the collision of a photon with a molecule, under conditions such that there is an interchange of some of the energy of the photon. The molecule absorbs the radiation and is raised to a higher energy level after which it emits radiation and sinks to a lower energy level but not necessarily to the energy level which it possessed in the initial state. After such a collision the scattered radiation has a slightly different frequency from that of the incident radiation, and there is a change in the energy of atomic oscillation within the molecule. Such a collision of a photon with a molecule may then be represented by the equation

$$h\nu_{\text{incident}} - h\nu_{\text{scattered}} = \text{Change in molecular energy} = h\nu_{\text{Raman}} \quad [20]$$

The difference in wave number between the incident and the scattered light permits a direct calculation of the Raman shifts. These frequency shifts are of the order of 100 to 4000  $\text{cm}^{-1}$ , and many of them are equal to frequencies found in infrared absorption. Usually the quantum imparts some of its energy to the molecule. The wave number of the

\* Bridgman, "The Logic of Modern Physics," The Macmillan Co., New York, 1927.

scattered light is then smaller than that of the incident light. It is possible, however, for a quantum of incident radiation to absorb a quantum from a molecule and leave with greater energy. In this case  $\nu_{\text{scattered}}$  is greater than  $\nu_{\text{incident}}$ .

Although the Raman lines may correspond to infrared lines, sometimes they correspond to transitions which are not directly allowed according to the restrictions of the quantum theory, i.e., to frequencies which do not occur in the ordinary absorption spectrum. Valuable information concerning the nature of the spectrum can thus be obtained by combining data from both the Raman and the absorption spectra.

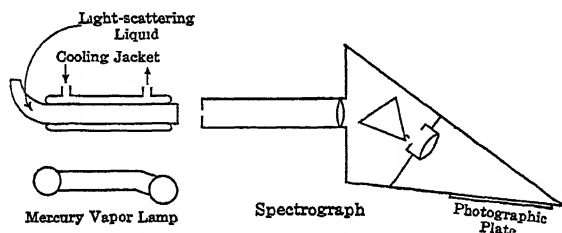


FIG. 144

Although this effect had been predicted by the quantum theory, it remained for Raman\* in 1928 to demonstrate that the scattered light does actually contain radiation of different frequency. The difficulty lay merely in giving long enough exposure to detect the feeble Raman lines which tend to be obliterated by light of the exciting frequency. The material is placed in front of a spectrograph slit and illuminated for a long exposure with a mercury-vapor lamp (using light filters), as shown in Fig. 144. The Raman spectrum of quartz, adapted from a photograph by Pringsheim, is shown in Fig. 145. On each side of the exciting line are seen lines which correspond to the infrared absorption lines indicated.

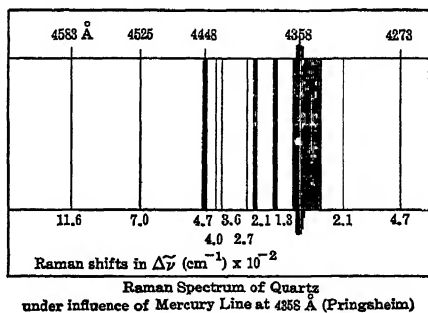


FIG. 145

Raman spectra have been measured for a great many organic and inorganic compounds, and complete reviews of this work are avail-

\*Raman, *Indian J. Phys.*, **2**, 387 (1928).

able.\* They are helpful in interpreting molecular structure and they are useful in analytical problems.

**Band Spectroscopy.** So many important subjects, including heats of dissociation, specific heats, entropies, atomic vibrations, inter-nuclear distances, intermediate compounds, and isotopes, can now be studied with the aid of band spectra that a further discussion seems justified, although a quantitative treatment is beyond the scope of

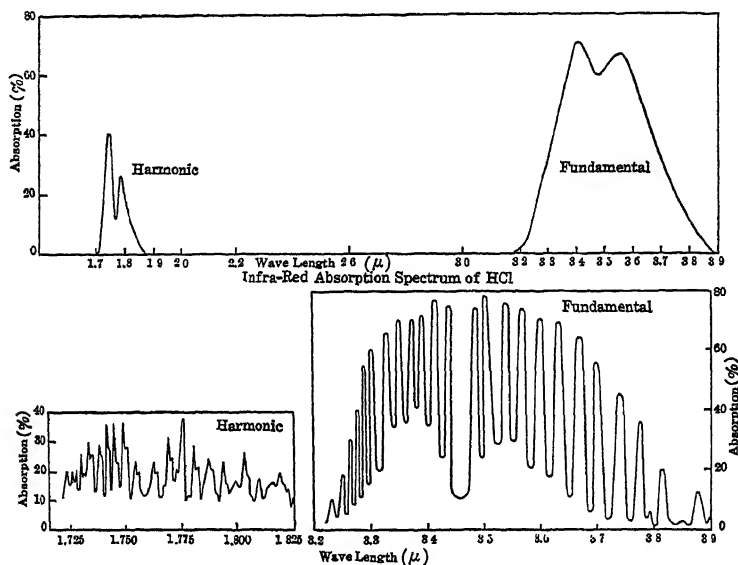


FIG. 146

this book. Absorption in the far infrared (50 to  $100\mu$ , for example) involves small quantities of energy, due to rotation of the molecule. Even here the energy absorbed is quantized and only certain quantities of energy can be absorbed, but the difference between them is very small. In the near infrared (1 to  $50\mu$ ) there is absorption by the displacement of atoms within the molecule, and the rotation spectrum is superimposed on the vibration spectrum, giving simple bands in the short infrared, such as are shown in Fig. 146† for hydrochloric acid.

\* Hibben, "Raman Spectra in Inorganic Chemistry," *Chem. Rev.*, **13**, 345-478 (1933); "Raman Spectra in Organic Chemistry," *Chem. Rev.*, **18**, 1-232 (1936); "The Raman Effect and Its Chemical Effects," Reinhold Publishing Corp., New York, 1939.

† Adapted from Brinsmade and Kemble, *Proc. Nat. Acad. Sci. U. S.*, **3**, 420 (1917); and Jones, *Astrophys. J.*, **50**, 251 (1919).

A diatomic molecule may be likened to a dumbbell, and Rayleigh showed that a rotating-vibrating molecule of this type having an electric moment should emit and absorb light of frequencies  $\nu_v \pm \nu_r$ , where  $\nu_v$  is the frequency of vibration and  $\nu_r$  is the frequency of rotation. When  $\nu_r = 0$ , the absorption is slight. A series of absorption lines is obtained by adding terms with quantum numbers of rotation 1, 2, 3, 4, etc., and a second series of lines is obtained by subtracting them. These two branches have maxima as indicated in Fig. 146. The distance between these maxima permits a calculation of the distance between the atomic nuclei in the molecule.

The bands recur at definite intervals ( $1.75$  and  $3.7\mu$  in HCl) which are governed by the integer multiples so common in quantum phenomena, except that small correcting terms are usually necessary. Under high dispersion the fine structure of the bands due to the quantized rotation of the molecule is apparent, as shown in the lower part of Fig. 146.

These rotation-vibration spectra are often superimposed, with some distortion, on spectra caused by electron displacements, giving band spectra in the visible and ultraviolet. The lines of the band due to changes in the energy of rotation come closer and closer together, forming the head of a band. The band of the compound CN, at  $4216 \text{ \AA}$ ., is sketched in Fig. 147.



FIG. 147

Combinations of these three factors — rotation, vibration, and electronic displacement — give very complex spectra, but in many cases they have been interpreted adequately.

The analysis of band spectra offers a powerful means for identifying materials present, either in emission spectra or absorption spectra.

Sometimes a spectrum has a number of discrete lines adjacent to a region of continuous absorption with a definite line of demarcation between the two. From the wavelength of this edge of the continuous spectrum it is possible to calculate the energy of dissociation of the molecule. Absorption spectra are discontinuous when the molecules are excited because the absorption is governed by quantum restrictions. However, when a molecule is dissociated, giving either normal atoms, excited atoms, or ions, the fragments are given a certain amount of kinetic energy which is not quantized. There are no limitations on the amount of energy which can then be utilized, and radiation of all wavelengths in the region is absorbed.

Accordingly, when the energy becomes great enough (the wavelengths are short enough) to cause dissociation, the absorption becomes



continuous. These phenomena are indicated in Fig. 148, where typical discrete lines corresponding to excitation are sketched at the right, heading into a band of continuous absorption at the left, corresponding to dissociation. The numbers refer to quantum numbers in the discontinuous spectrum. Just as the long-wavelength limit of continuous absorption in Fig. 140 permitted calculation of the energy of ionization of atoms, so also the long-wavelength limit of continuous absorption

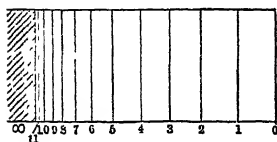


FIG. 148

in band spectra permits a calculation of the energy of dissociation of the molecule. These calculations may be illustrated in the case of chlorine, which dissociates into one normal atom and one excited atom. The continuous absorption, beginning at the convergence of the discontinuous lines, occurs at 4785 Å., which is equivalent to 59,400 cal. per mole. The extra energy of excitation of the atom corresponds to 2500 cal. as determined spectroscopically. The difference, 56,900 calories, is the energy required to disrupt the molecule, whereas direct thermal measurements give 57,000.

**Energy of Dissociation.** Dissociation energies can be obtained also from diagrams like that shown in Fig. 149, where the potential energy is plotted against the distance between atomic nuclei.\* Some atoms like helium repel each other at all distances; the potential energy is greatest when the atoms are close together, and it falls off gradually to zero when the atoms are far apart, as shown by the upper curve. In the case of most chemical substances the atomic nuclei repel each other at very close distances and attract each other at large distances, but the attraction becomes less as the distance becomes very great. This situation is represented by the lower curve in Fig. 149; it is obvious that there must be a minimum somewhere in the potential-energy curve. This minimum corresponds to the most stable condition of the molecule, and although the atoms oscillate back and forth in the molecule they tend to keep this distance corresponding to the minimum point.

The exact shapes of the curves ordinarily are not known but sometimes they can be determined from the data of band spectroscopy. They can be calculated with the empirical formula developed by Morse†

$$E = D'(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}) \quad [21]$$

where  $r_0$  is the distance separating the atoms in the normal molecule as

\* Franck, *Z. Physik*, **31**, 411 (1925).

† A discussion of this formula and others for calculating energies of diatomic molecules is given by Hirschfelder and Hulburt, *J. Chem. Phys.*, **9**, 61 (1941).

determined from x-ray or electron diffraction measurements, and  $D'$  is the energy of dissociation, as determined from spectroscopy or calorimetric measurements, together with the *zero point energy*.\* The

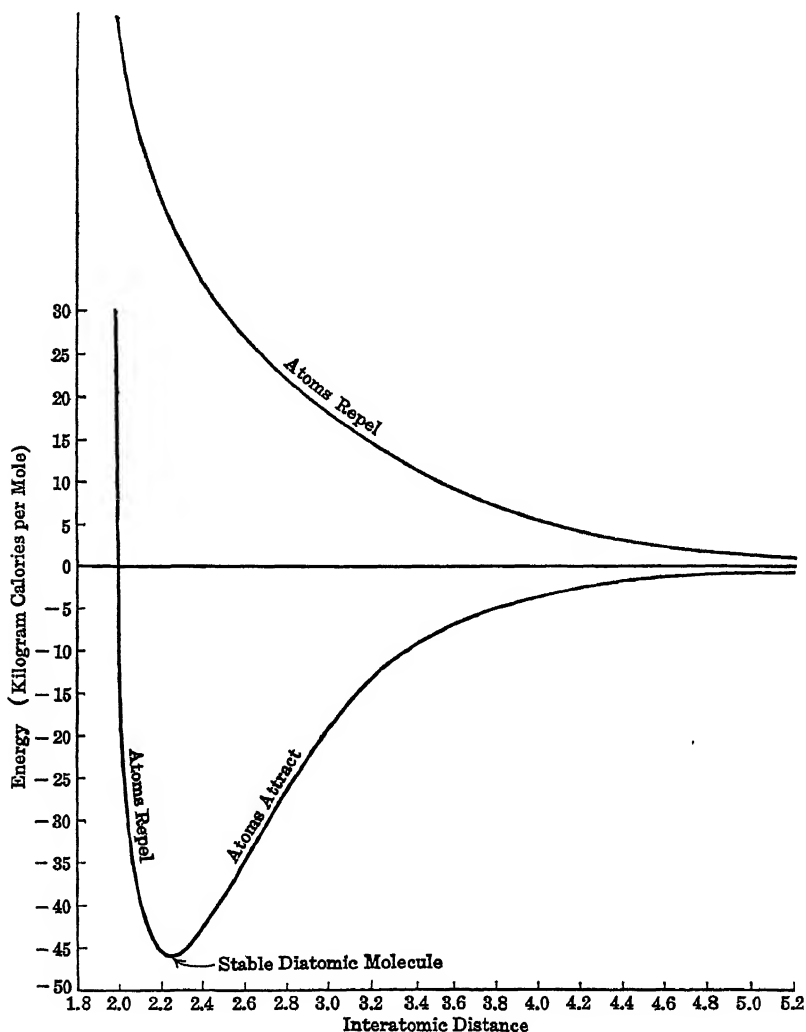


FIG. 149

\* The zero point energy is the half quantum of vibrational energy which the atom pair still possesses at absolute zero. The total energy of a linear harmonic oscillator is  $(n + \frac{1}{2}) h\nu$  where  $n$  is an integer (vibrational quantum number) and, since energy can be lost only as whole quanta,  $\frac{1}{2}h\nu_0$  remains, even at absolute zero where  $n = 0$ .

constant  $a$  depends on the normal vibration frequency of the atoms as determined from infrared absorption measurements or Raman spectra and on the atomic masses. When these quantities are known the energy  $E$  of the atom pair can be plotted against the distance  $r$  which separates the two atoms. A Morse curve is shown for the bromine molecule in Fig. 149.

**Quantum Mechanics.** The quantum theory is largely a theory of restrictions, and these restrictions have been determined empirically from laboratory measurements. Considerable attention was paid, therefore, to finding a theoretical foundation for these restrictions; Heisenberg and Born devised a theory based on matrix calculus and probabilities; De Broglie and Schrödinger developed a theory based on differential equations applied to waves; and Dirac embraced both in general terms with a new system of mathematics. Heisenberg's treatment and Schrödinger's treatment are both aspects of the same underlying principle, and, from both, the restrictions of the quantum theory come out automatically as mathematical necessities.

The Schrödinger wave equation for a simple particle is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad [22]$$

where  $m$  = mass of particle,  $V_{x,y,z}$  is its potential energy in a field of force, and  $E$  is its total energy, a constant. The quantity  $\psi$  is called the "wave function" because in many problems it exhibits a wave-like series of maxima and minima. Where  $|\psi|^2$  is large, there is a large concentration of electrons; in general,  $|\psi|^2$  determines the probability of an electron being in a specified region. When sufficient information is available,  $\psi$  can be determined by solving the differential equation (22). The wave function is usually continuous, single-valued, and finite; and zero at infinite distance. Solutions which meet these requirements are possible only when  $E$  is given certain characteristic values, and the corresponding solutions of  $\psi$  are called *characteristic solutions*.

These characteristic values give the stationary states of the Bohr atomic model, and thus the quantized energy levels come automatically from the Schrödinger wave equation.

Quantum mechanics is much superior to the older theories because, in addition to accomplishing all that they accomplished, it solves more complicated problems and in many cases gives better agreement with experiment. It has led to many new advances, only two of which will be mentioned here.

On the basis of the wave equations, electrons as well as radiation may be considered as waves. Davisson and Germer showed, in 1925, that streams of electrons do have properties attributed to waves and like x rays may be diffracted by a single crystal, and that the wave lengths depend on the voltage in agreement with theoretical calculations. There is evidence also that streams of hydrogen ions or protons have certain properties of waves and give diffraction patterns with a crystal lattice. It appears then that matter, electricity, and radiation are composed of discrete particles — atoms, electrons, and quanta. However, in all three cases a group of these particles taken together may exhibit the properties of waves.

One of the most striking achievements of quantum mechanics was the prediction that hydrogen should exist in two different forms, which are now called ortho- and para-hydrogen. It was predicted that the space wave functions of diatomic molecules with like nuclei can be either symmetric or antisymmetric, depending on the spins of the nuclei. Evidence for the two forms was found in band spectra, where alternate lines were missing or very weak, and in the abnormal specific heats of hydrogen at low pressures.

Bonhoeffer and Harteck\* succeeded in separating these two forms and in demonstrating the difference in specific heat and other properties. At room temperature ordinary hydrogen is a mixture of three parts of ortho-hydrogen (antisymmetric type) and one part of para-hydrogen (symmetric type); at the temperature of liquid air the equilibrium is approximately 1 to 1, and at the temperature of liquid hydrogen the ortho-hydrogen is not stable and goes almost entirely into the para- or symmetric form, when catalyzed with charcoal.

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\* Bonhoeffer and Harteck, *Z. physik. Chem.*, **43**, 113 (1929).

## PROBLEMS

1. A hollow box, with an opening of 1 sq. cm. area, is heated electrically.  
 (a) What is the total energy emitted per second at  $800^{\circ}\text{K}$ ?  
 (b) How much energy is emitted per second if the temperature is  $1600^{\circ}\text{K}$ ?  
 (c) How long would it take the radiant energy emitted at this temperature,  $1600^{\circ}\text{K}$ ., to melt 100 g. of ice?

*Ans.* (a)  $2.34 \times 10^7$  ergs  $\text{cm}^{-2} \text{sec}^{-1}$ ; (b)  $3.74 \times 10^8$  ergs  $\text{cm}^{-2} \text{sec}^{-1}$ ; (c) 890 sec.

2. Add 1.1 volt to values given in Fig. 142 and compare some of them with multiples of 4.9. (Other peaks involve multiples or combinations of a potential at 6.7.)

*Ans.* 4.9; 9.8; 14.7; 19.6.

3. Calculate the velocity of an electron which has been accelerated by a potential of 100 volts. The mass of an electron is  $9 \times 10^{-28}$  g. *Ans.*  $5.96 \times 10^8$  cm.  $\text{sec}^{-1}$ .

4. From the observed values of the critical potentials of hydrogen calculate:  
 (a) The wavelength of the first two lines of the Lyman series; (b) the wavelength of the first line of the Paschen series.

*Ans.* (a) 1216; 1024 Å. (b) 19,000 Å.

5. Show that the energy of a quantum of radiation in electron volts is equivalent to  $12,336 \div (\text{wavelength in Å})$ .

6. What is the wavelength of light emitted when electrons are stopped after falling through a potential of (a) 400 volts? (b) 3 volts?

*Ans.* (a) 30.8 Å. (b) 4112 Å.

7. An experiment on the emission of photoelectrons from a sodium surface gave the following values for the potentials at which the photoelectric current was reduced to zero:

(Å.)	<i>E</i> (volts)
5461	-2.045
4339	-1.488
4047	-1.295
3651	-0.914
3125	-0.382
2535	+0.52

Plot frequency against voltage, and determine Planck's constant from the slope of the line.

8. An electric heater of 30 sq. cm. is heated to  $800^{\circ}$ . How many calories of radiant heat is emitted per minute, assuming a perfect radiator?

9. Calculate the values of  $x$  and  $y$  in Table II.

10. Calculate  $\nu$ ,  $\bar{\nu}$ , and  $\lambda$  for the line in the Paschen series of the hydrogen spectrum which is due to a transition from the fifth quantum level to the third.

11. Calculate the velocity of an electron which has been accelerated in an x-ray tube by a voltage of 150,000 volts. The mass of an electron is  $9 \times 10^{-28}$  g.

12. Calculate the value of the constant  $\frac{300Rhc}{e}$  for hydrogen.

13. Assuming black-body radiation, how many calories per minute of radiant heat energy is emitted by a black object at  $100^{\circ}$  having a surface of 100 sq. cm.?

14. Calculate the wave length of the fifth line of the Balmer series for hydrogen.

15. Absorption by the fundamental vibration of the hydrochloric acid molecule occurs at  $3.64 \mu$ .

(a) What is the frequency of light of this wavelength?

(b) What is the energy of one quantum of light of this wavelength?

(c) What is the value of this wavelength in terms of electron volts?

(d) If it were possible for each molecule in 1 mole of HCl gas to absorb one quantum of energy at  $3.64 \mu$ , what would be the increase in energy of the gas in ergs? (Actually only a small fraction of the molecules absorb a quantum in a given second.)

16. Calculate the value of the Rydberg constant for hydrogen, and compare with the experimental value.

17. There is a Brackett series in the hydrogen spectrum where  $n_1 = 4$ . Calculate the wavelengths, in Ångström units, of the first two lines of this series.

18. Calculate the value of  $z$  in Table IV.

19. Electrons are accelerated by 100,000 volts in an x-ray tube. To what wavelength in Ångströms does this energy correspond, when converted into radiation?

20. Calculate the Morse curve for bromine given in Fig. 149. Referring to equation (20),  $D = 45.69$  kcal.;  $a = 1.98$ , and  $r_0 = 2.28 \text{ Å}$ .

21. The vibrational frequency  $V$  of a simple harmonic oscillator is given by

$V = \frac{1}{2\pi} \sqrt{\frac{f}{\mu}}$ , where  $f$  is the force of restitution on the vibrating particles and  $\mu$

is the reduced mass of the system. For a "dumbbell-shaped" diatomic molecule

$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$ , where  $m_1$  and  $m_2$  are the masses of the individual atoms. The fun-

damental frequency of the  $\text{HCl}^{35}$  molecule occurs at  $3.64 \mu$ . What would be the separation in Ångströms between the fundamental vibrations for  $\text{HCl}^{35}$  and  $\text{HCl}^{37}$  assuming that the forces of restitution are the same in both cases? Between  $\text{DCl}^{35}$  and  $\text{DCl}^{37}$ ? (The fundamental frequency of  $\text{DCl}^{35}$  is at  $4.8 \mu$ .)

## CHAPTER XX

### PHOTOCHEMISTRY

**Collisions between Molecules and Photons.** Photochemistry comprises the study of chemical reactions produced directly or indirectly by means of radiation.

It was shown on page 366 that molecular collision is the cause of ordinary chemical reactions. Only those molecules which contain an abnormal amount of energy can effect chemical reaction, and only a few molecules can obtain this energy from collision if the activation energy is large and the temperature low. Reactions of this type are necessarily slow.

It is possible, however, to activate molecules with an external source of energy, as for example, by introducing a beam of light having the proper frequency to be absorbed and a sufficient quantity of energy in each photon to effect the reaction. The idea underlying photo-

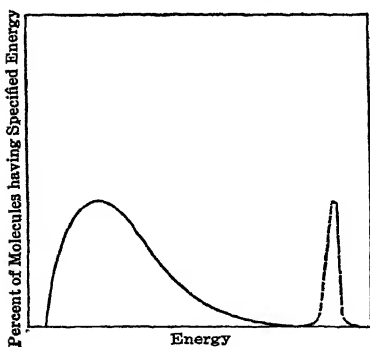


FIG. 150

chemical reactions induced by energy from an outside source is given in Fig. 150. The full line represents the distribution of energy among a group of molecules due to random collisions from heat. The number of molecules with high energy (at the right), sufficient for chemical reaction, is small. The dotted line represents the condition when a large number of high-energy molecules are produced by introducing a beam of light of the proper frequency. It is clear that the intensity

of light introduced does not depend on the temperature of the reaction vessel. Accordingly the primary process of photo-activation has a very low temperature coefficient in contradistinction to the large temperature coefficients of thermal reactions. If the overall photochemical reaction has a large temperature coefficient it may be concluded that there is included in the reaction at least one step which is an ordinary thermal reaction.

When a photon of radiation comes very close to a molecule several different things may happen. For transparent substances there is no

possible electronic, atomic, or molecular change which can use just the quantity of energy which is contained in the photon of radiation. Then there will be no interaction and no chemical or physical change. However, if there is within the molecule some change which is not in conflict with the quantum restrictions, and which corresponds to the energy of the photon, there may be a transfer of energy and the photon is "absorbed." Such a substance is not transparent. After a molecule has received this energy it may give it up on collision with other molecules thus increasing their kinetic energy. The total effect is thus the conversion of radiant energy into thermal energy and the raising of the temperature. This is the most common effect of the absorption of radiation.

The energy of a quantum may be transformed in several different ways as follows:

1. Heat. The temperature of the absorbing system is raised.
2. Dissociation. The molecule undergoes a chemical breakdown.
3. Excited molecule. The molecule retains its energy until it can be used chemically (a) by combination with some other molecule or (b) by transferring its energy to another molecule which in turn utilizes the energy to produce chemical change.
4. Dissociation and excitation. One of the dissociated fragments is excited.
5. Fluorescence. The excited molecule immediately reradiates part of the energy at a different wavelength.
6. Physical interaction. The quantum of radiation is not absorbed and re-emitted, but rather it (a) imparts some of its energy to an electron as explained by the Compton effect or (b) imparts some of its energy to atomic or molecular action as explained by the Raman effect.

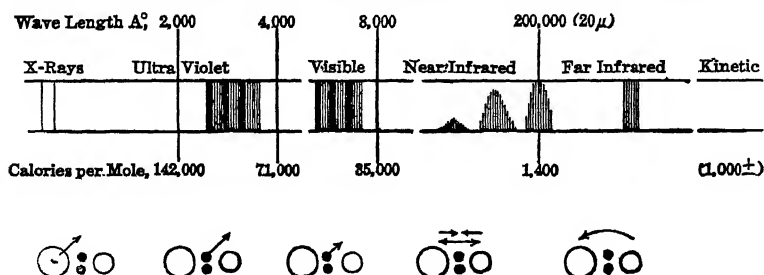


FIG. 151

**Types of Spectra.** A molecule may be excited in several different ways depending on the varying frequency of radiation absorbed. These different methods of absorbing radiation in the different parts of the spectrum and the energies involved are summarized in Fig. 151.



In the upper half of the figure are given the general types of spectra together with the wavelength regions and the energy of the radiation in calories per mole. In the lower part is given a crude representation of what happens when the radiation is absorbed. The black dots represent electrons, and the larger circles represent atoms in the molecule. The same general considerations apply to polyatomic as well as to diatomic molecules. All the intramolecular changes involve definite energy increments which are governed by the quantum theory.

Absorption in the far infrared causes the molecule to rotate as indicated by the curved arrow at the right. The energy involved in these operations is of the order of a thousand calories per mole.

This is the only operation which can be carried out with energies of this magnitude and so there are definite lines corresponding to quantum numbers. Absorption in the near infrared displaces atoms from their normal positions and causes them to oscillate back and forth or to move sidewise with a swinging motion within the molecule. These operations involve energies between about 1000 and 30,000 to 40,000 cal. The rotations, involving small energies, are superimposed upon the atomic displacements, giving rise to absorption bands. The intramolecular changes can be combined so as to give harmonics absorbing approximately twice or three times, etc., the energy, and causing absorption bands at half and one-third the wavelength. The probability of absorbing energy corresponding to two or three or more quanta is less than the probability of absorbing one, and so the fundamental band (the one-quantum operation) is the most prominent, with the absorption becoming progressively less intense at the higher harmonics. This decrease in intensity at the shorter wavelengths is represented diagrammatically by reducing the height of the bands.

In the visible and ultraviolet region of the spectrum the absorption consists in displacing an outer electron in the molecule. The only difference between the ultraviolet and visible spectra is that greater energies and larger displacements are involved in the ultraviolet absorption — 35,000 to 71,000 cal. per mole being required for absorption in the visible region and 71,000 to several hundred thousand for absorption in the ultraviolet. In these regions series of bands may be obtained by combining the energies of the three quantum-restricted operations — electron displacement, atomic displacement, and molecular rotation.

In the x-ray region of very short wavelengths (about  $1 \text{ \AA}$ .), the electrons deep inside the atom (nearest the nucleus) are displaced.

Energies of the order of hundreds of millions of calories per mole are required for these displacements.

If the energies of radiation or of suitable projectiles, such as alpha particles, are increased to a still greater order of magnitude (around  $10^{10}$  cal. per mole) it is then possible to affect the nucleus of atoms and produce the transmutation of elements.

The various absorption spectra, produced by the displacements indicated in Fig. 151, are usually the same as the emission spectra produced when the electrons or atoms return to their normal positions, or when the molecules are caused to rotate by collisions or other means.

At the extreme right of Fig. 151 is given for comparison the order of magnitude of the average kinetic energy of molecular translation  $\frac{3}{2}(RT)$ , a few hundred calories.

It will be remembered from page 377 that the energies of most chemical reactions range from about 10,000 to 100,000 cal. It is evident, then, that the longer infrared radiation is powerless to produce chemical reaction and that x rays contain so much energy that they are more likely to accomplish chemical reactions through secondary effects. Visible light and particularly ultraviolet light are, then, of chief interest in photochemistry.

**Laws of Photochemistry.** The first law of photochemistry was enunciated by Grotthus in 1818. It seems obvious that *only those rays of light which are absorbed can produce chemical change*. It does not follow, however, that chemical action must accompany the absorption of light.

The Einstein law of photochemical equivalence has become the guiding principle in the theoretical interpretation of photochemical reactions. According to this law, *in the primary photochemical process each molecule is activated by the absorption of 1 quantum of radiation*.

In this simple, primary process, then, we should find that the number of molecules activated is exactly equivalent to the number of quanta absorbed, and for a gram-molecule of  $6.02 \times 10^{23}$  molecules there should be  $6.02 \times 10^{23}$  quanta absorbed. This "gram-molecule" of quanta has been called the "einstein," just as a gram-equivalent of electrons ( $6.02 \times 10^{23}$  electrons or 96,500 coulombs) is called the faraday.

It must be strongly emphasized that the Einstein law is usually masked by secondary reactions and complicating circumstances which prevent a simple 1 to 1 relationship between the number of quanta absorbed and the number of molecules of *final* products in the reaction. Most investigators are inclined to accept the law and

to look for the complicating circumstances which are peculiar to each particular reaction. Sometimes the activation process is followed by a simple stoichiometric reaction which gives some simple number, such as 2 molecules per quantum, or by a series of repeated reactions giving rise to a chain reaction. On the other hand, the activated molecules may be partially deactivated by collisions or by fluorescence or by internal rearrangements and loss as heat. Again, dissociated fragments resulting from the excitation may recombine so as to give low apparent yields. The quantum yield  $\Phi$  is given by the expression

$$\Phi = \frac{\text{Numbers of molecules reacting chemically}}{\text{Numbers of quanta absorbed}} \quad [1]$$

It will be remembered that the energy in one quantum of radiation is given by the fundamental quantum relation

$$\epsilon = h\nu \quad [2]$$

The energy per *einstein*, i.e., per mole of photons, is obtained by multiplying this equation by the Avogadro number  $N$

$$Nh\nu = 6.02 \times 10^{23} \times 6.62 \times 10^{-27}\nu \quad [3]$$

The frequency of radiation  $\nu$  is related to the wavelength  $\lambda$  and the velocity of light  $c$  ( $3 \times 10^{10}$  cm./sec.<sup>-1</sup>) by the relation

$$\nu = \frac{c}{\lambda} \quad [4]$$

*Example 1.* Calculate the frequency of ultraviolet light, having a wavelength of 3000 Å.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^{10}}{3000 \times 10^{-8}} = \frac{3.00 \times 10^{10}}{3 \times 10^{-5}} = 1 \times 10^{15}$$

Calculate the energy in ergs per quantum and calories per "mole" in radiation of this frequency

$$\epsilon = h\nu = 6.62 \times 10^{-27} \times 1 \times 10^{15} = 6.62 \times 10^{-12} \text{ erg}$$

$$Nh\nu = 6.02 \times 10^{23} \times 6.62 \times 10^{-27} \times 1 \times 10^{15} = 3.98 \times 10^{12} \text{ ergs per mole}$$

$$= \frac{3.98 \times 10^{12}}{4.183 \times 10^7} = 95,270 \text{ cal. per mole}$$

The energy associated with quanta of typical wavelengths is given in Table I on page 582.

It is so often necessary to convert wavelengths and energies into different units that the graphs given in Figs. 152 and 153 are convenient.

In Fig. 152 kilogram-calories per mole are plotted against wavelengths in Ångström units on the upper curved line and against fre-

quencies  $\nu$  or wave numbers  $\tilde{\nu}$  on the upper straight line. For example, 4000 Å. intersects the kilogram-calorie curve at 71,000 (in agreement with Table I) and the volt curve at 3 volts. Again, a

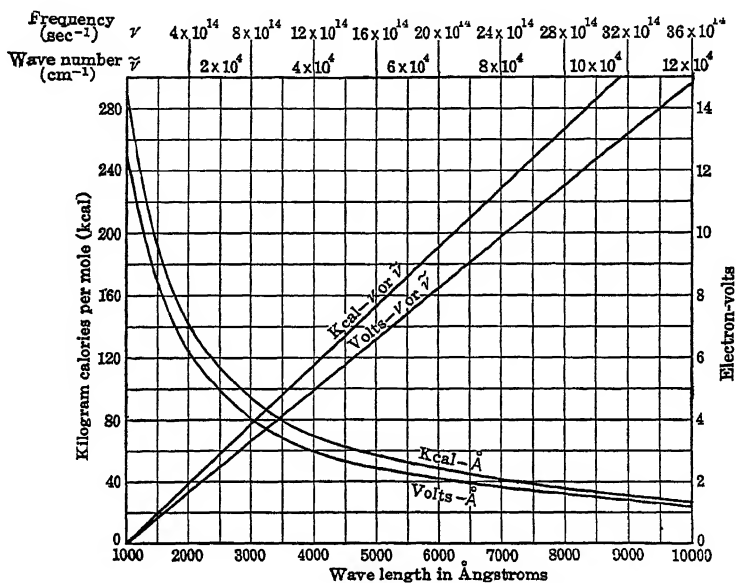


FIG. 152

frequency  $\nu$  of  $12 \times 10^{14}$  or a wave number  $\tilde{\nu}$  of 40,000 corresponds to 116 kcal.; or to 5 volts. It is possible to convert Ångströms to frequencies or kilogram-calories to volts by shifting from one curve

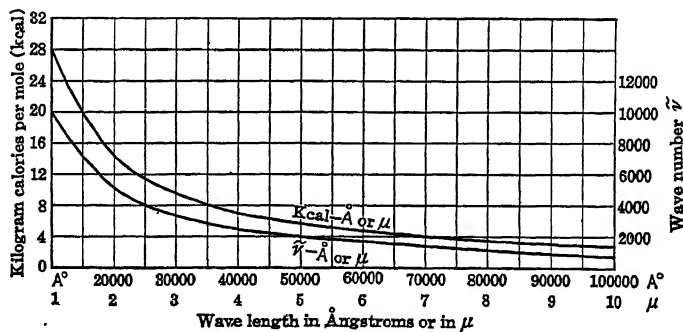


FIG. 153

to the other. Thus the intersection on  $\nu$  of  $12 \times 10^{14}$  gives 116 kcal., and passing to the curve at the left 116 kcal. corresponds to a little less than 2500 Å.

TABLE I  
ENERGY OF DIFFERENT RADIATIONS

Wavelength, Å.	Frequency, $\nu$	Approximate Color	Energy of 1 quantum $h\nu$ in ergs	Energy of 1 einstein in calories per mole
10,000	$3 \times 10^{14}$	Short infrared	$1.986 \times 10^{-12}$	28,580
8,000	$3.75 \times 10^{14}$	Edge of visible	$2.48 \times 10^{-12}$	35,730
7,000	$4.29 \times 10^{14}$	Red	$2.84 \times 10^{-12}$	40,840
6,200	$4.85 \times 10^{14}$	Orange	$3.20 \times 10^{-12}$	46,100
5,800	$5.19 \times 10^{14}$	Yellow	$3.42 \times 10^{-12}$	49,280
5,300	$5.76 \times 10^{14}$	Green	$3.74 \times 10^{-12}$	53,930
4,700	$6.40 \times 10^{14}$	Blue	$x$	$y$
4,200	$7.15 \times 10^{14}$	Violet	$4.73 \times 10^{-12}$	68,050
4,000	$7.5 \times 10^{14}$	Edge of visible	$4.96 \times 10^{-12}$	71,460
3,000	$1 \times 10^{15}$	Ultraviolet	$6.62 \times 10^{-12}$	95,270
2,000	$1.5 \times 10^{15}$	Ultraviolet	$9.93 \times 10^{-12}$	142,900
1,000	$3 \times 10^{15}$	Ultraviolet	$1.99 \times 10^{-11}$	285,800
1	$3 \times 10^{18}$	X rays	$1.99 \times 10^{-8}$	$2.86 \times 10^8$

The scale shown in Fig. 153 is useful for infrared spectroscopy. It enables one to convert wavelengths in Ångström units or in microns, directly into kilogram-calories, using the upper curve, or into wave numbers, using the lower curve.

**Experimental Procedure.\*** In quantitative photochemical investigations it is best to use light of a narrow range of wavelengths and to measure the intensity of light absorbed. The photochemical reactions are influenced by both intensity and wavelength, and it is necessary to separate the two factors.

The intensity of radiation is measured with a thermopile, which consists of a series of junctions of unlike metals, such as bismuth and silver or copper and constantan connected to a galvanometer. Alternate junctions are heated by exposure to the radiation, and the galvanometer deflections are proportional to the intensity of radiation. The junctions are covered with blackened metal strips of very low heat capacity, which convert radiation of all wavelengths directly into heat. The galvanometer readings may be converted into ergs of radiation per second per square millimeter striking the thermopile, by calibrating with a standard carbon filament lamp from the U. S. Bureau of Standards.

\* Noyes and Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, 1941, Chapter II; Daniels, Mathews, and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., New York, 1941, Chapters XV and XXVII; Daniels, *J. Phys. Chem.*, **42**, 701 (1938).

The light can be restricted to a narrow range of wavelengths with the help of properly chosen filters which absorb the undesired wavelengths. The separation may be effected still better by refraction through a prism in a monochromator; the best results are obtained with a source of light like a mercury-vapor lamp which gives a discontinuous spectrum. Under these conditions a single spectral line may be isolated for the photochemical reaction. The intensity obtainable with a monochromator is very low, and it is necessary to use capillary arcs or other very intense sources of light, and to employ prisms and lenses of large dimensions in order to obtain sufficient intensity for investigating photochemical reactions. The reacting system is placed in glass or quartz vessels provided with clear, polished windows, and the light is usually passed through the cell onto the thermopile. The actual energy absorbed in the reacting system is measured by subtracting these thermopile readings from those obtained when the cell is empty, or filled with a transparent solvent. It is a still better plan to use two identical cells.

Failure to control the wavelength and intensity may lead to erroneous conclusions. For example, when a certain reaction is exposed to sunlight through a red filter it may proceed faster than when exposed through a blue filter. But red light is present in sunlight in much greater intensity than the blue, and one cannot conclude that the greater effect is due to the color; it may be due to the greater intensity. As another example, one may cite the action of the mercury-vapor lamp in producing ozone from oxygen. Ozone is synthesized by the short ultraviolet and decomposed by longer ultraviolet (2800 Å.). The actual yield of ozone depends then on the ratio of the intensities in these two regions, and this ratio depends on accidental conditions such as the age and the rate of cooling of the lamp. Experimental checks under such uncontrolled conditions cannot be expected.

In quantitative work where a knowledge of the reaction mechanism and rate is needed it is not sufficient to place the reaction cell in front of a source of light. The reaction may slow down as the material is consumed not only on account of the mass law but also on account of the lessened absorption of light. The number of calories of radiation, or better the number of photons actually absorbed, is the significant thing. The number of molecules can be determined by chemical or physical analysis and the ratio of molecules reacting per photon absorbed, can be readily calculated. This is the quantum yield  $\Phi$  as already defined.

The intensity of light available for photochemical reactions is measured most accurately with a thermopile, but with limitations it may sometimes be measured with a photoelectric cell or by the amount

of photochemical reaction produced in an *actinometer*. It is necessary to calibrate these other measuring devices against a thermopile. The blackened receivers of a thermopile are equally responsive to all wavelengths, whereas photoelectric cells and the actinometers are selective.

The uranyl oxalate actinometer, studied with great accuracy by Leighton and Forbes,\* is the best for most purposes. Although the quantum efficiency changes slightly with the wavelength, it may be assumed that, in a solution  $M/100$  in  $\text{UO}_2\text{SO}_4$  and  $M/20$  in  $\text{H}_2\text{C}_2\text{O}_4$ , 0.57 molecule of the oxalic acid is decomposed for each quantum of light absorbed between the wavelengths 2540 and 4350 Å. In other words, each mole of oxalic acid decomposed is equivalent to 1.75 einstein, or to 166,000 cal., assuming an average wavelength of 3000 Å. The uranyl ion undergoes no chemical change.

For very low light intensities photoelectric cells and Geiger-Müller counters (page 601) are useful, but in photochemical work it is usually the sensitivity of the chemical tests rather than the sensitivity of the radiation measurement which limits the accuracy.

**Photochemical Kinetics.** The kinetics of photochemical reactions is more complicated than the kinetics of thermal reactions because more variables are involved. The intensity of light and the size and shape of the vessel may affect greatly the rate of the reaction. A photochemical reaction may be accompanied by a thermal reaction, identical with the photochemical reaction, or opposite to it, or entirely different in character. A photochemical reaction may produce a catalyst which then causes a thermal reaction to proceed at a measurable rate. Sometimes an *induction period* is necessary while a sufficient quantity of catalyst is being accumulated to make the reaction proceed with a measurable velocity. Again a thermal reaction once started may continue after the illumination is stopped, giving an *aftereffect*. The energy available in a photochemical reaction is much greater than in the thermal reaction, and this fact often changes the character of the reaction. For example, the thermal dissociation of hydriodic acid at  $450^\circ$  is bimolecular ( $2\text{HI} = \text{H}_2 + \text{I}_2$ ), but the photochemical reaction is unimolecular ( $\text{HI} = \text{H} + \text{I}$ ) because it can provide the extra energy required to produce free atoms.

Not only second-order and first-order reactions, but zero-order reactions, also, are found in photochemistry. A zero-order reaction is one in which the rate is entirely independent of the concentration. For example, if the concentration is high and the light intensity is weak, the light intensity may be the limiting factor in the reaction rate and the concentration may be without influence on the rate.

\* Leighton and Forbes, *J. Am. Chem. Soc.*, **52**, 3139 (1930).

If the reaction cell is shallow, the absorption of light is slight, so that practically all parts of the reacting system have about the same illumination, and stirring becomes unimportant. If, on the other hand, the light is largely absorbed in the first portion of the reacting system, the extent of the reaction will vary with the depth, and vigorous stirring may be necessary to give uniform and reproducible conditions.

If light causes a reaction in one direction, giving a zero-order reaction, and a thermal reaction occurs in the opposite direction proportional to the concentration of the photochemical product, a stationary state will eventually be produced in which the two rates are exactly equal. The situation is described mathematically by the following equation:

$$\frac{dx}{dt} = k_{\text{photo}}I - k_{\text{thermal}}x \quad [5]$$

where  $k_{\text{photo}}$  and  $k_{\text{thermal}}$  are the specific reaction rates of the photochemical and thermal reactions and  $x$  is the amount of material produced by the photochemical reaction. At equilibrium

$$k_{\text{photo}}I = k_{\text{thermal}}x, \quad \text{and} \quad x = \frac{k_{\text{photo}}I}{k_{\text{thermal}}} \quad [6]$$

The concentration of material in the stationary state changes with the intensity of the light. An example of this type of reaction is the photopolymerization of anthracene, dissolved in xylene. In the presence of ultraviolet light this substance forms dianthracene which has twice the molecular weight of anthracene, but in the dark the dianthracene is depolymerized, giving the original anthracene.

The experimental determination of the quantum yield constitutes an excellent method for studying *chain reactions* (page 384). If several molecules of products are formed for each quantum of light absorbed, the reaction is obviously a chain reaction in which the products of the reaction are able to activate additional molecules of reactants.

The photocombination of hydrogen and chlorine is a classical example of such a reaction, about a million molecules reacting for each quantum absorbed. Each molecule of hydrochloric acid formed undergoes further reaction with the hydrogen and chlorine atoms produced (page 384). The measurement of the number of molecules per quantum gives a measure of the average number of molecules involved in the chain.

Examples of chemical chain reactions were given on pages 384 and 386 and the photochemical chains can be given in the same way except that a term is added to describe the rate at which photons of light are absorbed by the reacting system for the first step in the chain.



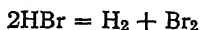
In studying the kinetics of a photochemical reaction it is desirable to express the experimental facts in a simple way by stating the quantum yield. The amount of reaction may vary with the intensity of light, the length of the cell, the concentration of the reactants, and many other factors, but the ratio of molecules reacting per quantum provides a good description under a specified set of conditions and gives considerable information regarding the process. For further information it is desirable to determine the influence of concentration and thus establish the order of the reaction, to determine the influence of temperature and thus ascertain whether or not thermal reactions are playing an important part, and to determine the influence of light intensity. If the quantum yield changes with the light intensity (i.e., the amount of the reaction is not directly proportional to the intensity of light absorbed) it may be concluded that the light intensity is not the limiting factor or that more than one reacting molecule or fragment is produced by the light, each in turn taking part in secondary reactions.

Writing a rate equation for the photochemical reaction, including a term for the intensity of the light, describes most comprehensively the facts of a photochemical reaction. Although these expressions may be largely empirical they frequently reveal much concerning the true mechanism of the reaction.

*Example 2.* The following reactions describe the photochemical decomposition of hydrogen bromide with light of 2530 Å. at 25°. The primary process disrupts the molecule into atoms of hydrogen and bromine which can then undergo further reactions. The quantum yield for the primary process is sometimes designated by  $\phi$ , whereas the quantum yield for the overall reaction is designated by  $\Phi$ . The intensity of light absorbed is designated by  $I$ .

- |   |   |
|---|---|
| (1) $\text{HBr} + h\nu = \text{H} + \text{Br}$        | Rate = $\phi I$                           |
| (2) $\text{H} + \text{HBr} = \text{H}_2 + \text{Br}$  | Rate = $k_2 C_{\text{H}} C_{\text{HBr}}$  |
| (3) $\text{Br} + \text{Br} + (M) = \text{Br}_2 + (M)$ | Rate = $k_3 C_{\text{Br}}^2 C_M$          |
| (4) $\text{H} + \text{Br}_2 = \text{HBr} + \text{Br}$ | Rate = $k_4 C_{\text{H}} C_{\text{Br}_2}$ |

The overall reaction is



Reaction (3) describing the recombination of bromine atoms requires a collision with a wall or a third molecule  $M$  in order to dissipate the heat of combination and permit the two atoms to remain united.

Other reactions might be written on paper, such as  $\text{Br} + \text{HBr} = \text{Br}_2 + \text{H}$  and  $\text{Br} + \text{H}_2 = \text{HBr} + \text{H}$ , but they require so much energy for activation that they do not proceed at room temperature and may be neglected.

As the bromine accumulates, reaction (4) becomes important and reduces the quantum yield.

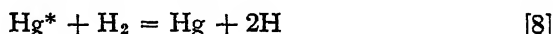
These facts can be summarized by the expression for the disappearance of hydrogen bromide:

$$\Phi = \phi + \phi \frac{1 - k_4 C_{Br_2} / k_2 C_{HBr}}{1 + k_4 C_{Br_2} / k_2 C_{HBr}}$$

When the concentration of bromine is zero (at the beginning of the illumination or when mercury or other bromine acceptor is added).

$$\Phi = 2 \phi \approx 2$$

**Photosensitization.** Very often the molecules which absorb the light take part in the photochemical reaction only in an indirect manner and act merely as carriers of energy. One of the outstanding examples is that of mercury vapor, activated by the absorption of ultraviolet light of 2536.7 Å. which is emitted by a mercury-vapor lamp. The energy corresponding to this radiation is very large (112,000 cal.), and it is more than the 102,400 cal. necessary to dissociate hydrogen molecules. When mercury vapor is mixed with hydrogen and exposed to light from a mercury-vapor lamp, the chief reactions may be represented by the following equations, where  $Hg^*$  represents an activated mercury atom:



The mercury acts as a photosensitizer, and the hydrogen atoms readily reduce metallic oxides, nitrous oxide, ethylene, carbon monoxide, and other materials. The excited mercury atoms decompose not only hydrogen but also ammonia and many different organic compounds.\*

The photodecomposition of oxalic acid, sensitized by uranyl ion, has already been referred to as a reproducible reaction suitable for use as an actinometer. The light is absorbed by the colored uranyl ion and the energy is transferred to the colorless oxalic acid which then decomposes. The uranyl ion remains unchanged and can be used over and over again indefinitely as a sensitizer. It is probable that some kind of an "energy-bridge," or loose chemical compound, or "complex" must be formed in order that this energy may be transferred. Supporting this view is the fact that the absorption of light is increased somewhat by adding colorless oxalic acid to a solution of uranyl ion. This change in absorption of light on mixing is one method by which chemical interaction of solutes (or gases) can be detected. Uranyl

\* Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931, pp. 1480-1482.

ion and light will not bring about chemical reaction in all substances even if the light energy is sufficient. Apparently the transfer of energy during an ordinary instantaneous collision is not often possible; some kind of a loose, or temporary chemical combination is helpful in giving favorable conditions for the transfer.

**Typical Reactions.** A few typical photochemical reactions\* are summarized in Table II.

TABLE II  
QUANTUM YIELDS IN PHOTOCHEMICAL REACTIONS AT ROOM TEMPERATURE

Reaction	Approximate Wavelength Region in Ångström Units	Approximate $\Phi$
1. $\text{HI} = \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{I}_2$	3000-2800	1
2. $\text{S}_2\text{O}_3^{--} + \text{H}_2\text{O} = 2\text{SO}_3^{--} + 2\text{H}^+ + \frac{1}{2}\text{O}_2$	3000-2500	1
3. $\text{C}_{14}\text{H}_{10} \rightleftharpoons \frac{1}{2}(\text{C}_{14}\text{H}_{10})_2$	<3600	1-0
4. $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$	4350	0
	4050	0.7
	3660	1.5 (2)
5. $\text{CH}_3\text{CHO} \rightarrow \text{CO} + \text{CH}_4 (+\text{C}_2\text{H}_6 + \text{H}_2)$	3100	0.5
	2537	1
6. $(\text{CH}_3)_2\text{CO} \rightarrow \text{CO} + \text{C}_2\text{H}_6 (+\text{CH}_4)$	<3300	0.2
7. Crotonic aldehyde	<3100	0.0
8. $\text{NH}_3 \rightarrow \frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2$	2100	0.2
9. $\text{H}_2\text{C}_2\text{O}_4 (+\text{UO}_2^{--}) \rightarrow \text{CO} + \text{CO}_2 + \text{H}_2\text{O} (+\text{UO}_2^{--})$	4300-2500	0.5-0.6
10. $2\text{NO}_3^- \rightarrow 2\text{NO}_2^- + \text{O}_2$	3000-2500	0.01-0.3
11. $\text{Cl}_2 + \text{H}_2 \rightarrow 2\text{HCl}$	4000	$10^6$
12. $\text{Br}_2 + \text{C}_6\text{H}_5\text{CH}=\text{CHCOOH} \rightarrow \text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{Br}_2\text{COOH}$	<5500	100-1
13. $\text{C}_2\text{H}_2 \rightarrow \frac{1}{n}(\text{C}_2\text{H}_2)_n$	2000	7
14. $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$	4000-4360	1000

Reactions 1 to 4 have quantum yields of nearly unity, indicating that the primary photoprocess is not followed by secondary reactions or rearrangements. Reaction 1 is one of the simplest photochemical reactions, and it has the same value of  $\Phi$  from 2800 to 3000 Å., at low pressures and high pressures, in the liquid state or in solution in hexane. Reaction 3 has a quantum yield of unity initially, but the reverse

\* Noyes and Leighton, "Photochemistry of Gases," Reinhold Publishing Corp., New York, 1941, appendices, pp. 415-465; Daniels, *J. Phys. Chem.*, **41**, 713 (1938).

thermal reaction reduces it as the product accumulates. In reaction 4 at 3660 Å. the photoprocess is completely efficient ( $\Phi = 2$ ) if correction is made for internal screening by the accompanying  $N_2O_4$  which absorbs some of the light. The reactions are  $NO_2 + h\nu = NO_2^*$ ,  $NO_2^* + NO_2 = 2NO + O_2$  where the asterisk indicates an activated molecule. At longer wavelengths the spectrum is of a different type, and at 4350 Å. no reaction occurs when the radiation is absorbed.

Reaction 5 likewise shows a greater photochemical efficiency at the shorter wavelengths where the absorption spectrum is different. This reaction is interesting because at 300°  $\Phi$  has a value of more than 300 indicating that the free radicals which are first produced by the absorption of light are able to propagate a chain reaction at the higher temperatures.

In reaction 6 the primary reaction is probably  $CH_3COCH_3 + h\nu \rightleftharpoons CH_3 + COCH_3$ . The acetyl radical can then decompose into CO and  $CH_3$  or it can react with  $CH_3$  to give back acetone. At room temperature it forms biacetyl  $(COCH_3)_2$ . In crotonaldehyde, reaction 7, no photochemical decomposition is observed.

In the photolysis of ammonia, reaction 8, hydrogen atoms are split off and the low yield is probably due to partial recombination of the fragments. The quantum yield varies with pressure and reaches a maximum at 80–90 mm.

Reaction 9 illustrates a photosensitized reaction. Reaction 10 is complicated and depends on the pH of the solution. It is more efficient at the shorter wavelengths. Reaction 11 is the best-known example of a chain reaction, and it is one of the longest chains. Oxygen and certain other substances act as inhibitors by combining with the chlorine or hydrogen atoms, thus stopping the propagation of the chain and reducing the quantum yield.

The addition of bromine to cinnamic acid, reaction 12, is a chain reaction the length of which depends on the temperature and the concentration of bromine and the amount of dissolved oxygen. The reaction can be split up into the primary photoprocess, which is not affected by temperature, and the subsequent thermal reaction which has a large temperature coefficient. When oxygen is removed the breaking of chains is less frequent and the quantum yield is of the order of hundreds and more. In some other photochemical reactions oxygen increases the reaction rate.

The polymerization of acetylene, reaction 13, to give an insoluble substance called cuprene, is effected by short ultraviolet light with a quantum yield of about 7 showing that the primary process is followed by a short chain reaction.

Reaction 14 varies with the pressures of carbon monoxide and chlorine, and, like all chain reactions, is sensitive to impurities.\*

**Luminescence.** When a solid body, a bar of iron for example, is heated to about 500°, it becomes "red hot"; when the temperature is raised still higher, it becomes "white hot," as the wavelengths of maximum intensity shift toward the shorter end of the spectrum in accordance with Wien's displacement law. It is possible, however, to produce light by other agencies than heat, and the radiation thus produced is called *luminescence* or sometimes "cold light." In all cases the emission of visible light may be attributed to the return of an outer electron toward its normal position after being displaced by kinetic bombardment of atoms and molecules, or by chemical or electrical or other forms of energy.

*Chemiluminescence* is the emission of light by certain chemical reactions. Thus Evans and Dufford† have shown that the oxidation of ether solutions of magnesium *p*-bromophenyl bromide gives rise to marked chemiluminescence, the greenish-blue glow which accompanies the exposure of the solution to air being visible in daylight. The oxidation of decaying wood containing certain forms of bacteria, of luciferin in fireflies, and of yellow phosphorus are further examples.

*Fluorescence* is the emission of light by molecules or atoms which have been excited by the absorption of light, the fluorescent light having a wavelength different from that of the incident radiation. In general, the wavelength of the transformed radiation is greater than that of the incident radiation. This relation, to which numerous exceptions have been discovered, was first enunciated by Stokes. When the incident radiation is cut off, fluorescence ceases.

Among the numerous substances which are known to exhibit the phenomenon of fluorescence may be mentioned fluorite (from which the phenomenon derived its name), uranium glass, petroleum, solutions of certain organic dyestuffs, eosin, fluorescein, quinine sulfate, chlorophyll, and the vapors of sodium, mercury, iodine, and acetone.

The characteristic fluorescence of various substances when exposed to the invisible ultraviolet light provides an effective means of analysis in many cases.‡ Moreover, the intensity of fluorescence can be used for quantitative analysis. For example, the concentration of ribo-

\* Further details of facts and theories for these and other photochemical reactions may be found in Noyes and Leighton, *loc. cit.*

† Evans and Dufford, *J. Am. Chem. Soc.*, **45**, 278 (1923).

‡ Radley and Grant, "Fluorescence Analysis in Ultraviolet Light," D. Van Nostrand Co., New York, 1933.

flavin in chloroform is determined by this method. The fluorescence produced by x rays falling on a film of barium platinocyanide or other material is the principle of the fluoroscope used in x-ray diagnosis.

There are also many substances known which continue to emit light for some time after the external light stimulus is removed. This phenomenon is termed *phosphorescence*. The sulfides of the alkaline earths may be mentioned as examples of phosphorescent substances. A trace of one of the heavy metals greatly intensifies the light emitted by a phosphorescent substance. Usually impurities, in the form of mixed crystals, are necessary for phosphorescence. Many different colors are now available among the phosphorescent compounds.

Bombardment by electrons produces luminescence in rarefied gases at low pressures and in certain organic and inorganic crystals. The amount of visible fluorescence produced by a given input of energy may be great. This is the basis of the development of "fluorescent" lighting. Alpha particles from radioactive elements produce bright luminescence when they hit a screen of zinc sulfide. Luminescent paints for watch dials are made by mixing the zinc sulfide and the radioactive material together with a binder.

**Photography.** If silver chloride or bromide is mixed with gelatin and given a very brief exposure to light, no change can be detected; but when it is immersed in a solution of a mild reducing agent, such, for example, as pyrogalllic acid, the parts which have been exposed to light are developed, that is, they are reduced to metallic silver much more rapidly than the unexposed parts. The photographic plate consists of a large number of minute grains of crystalline silver halide; some of these grains are completely reduced by the developer to black metallic silver, and others are unaffected. Apparently it is necessary for a quantum of energy to strike a sensitive spot in the crystal lattice in order that the silver halide may be reduced to give a nucleus of silver which then spreads, on further reduction, to include the whole grain.\* These sensitive spots seem to be identified with minute impurities of silver sulfide in the crystal lattice which are particularly responsive to the action of light. By increasing the number of these sensitive spots and by other means the speed of photographic films and plates has been greatly increased, i.e., satisfactory photographs can be made with much weaker light than was possible heretofore.

The camera and lens focus the image of the object on the photographic plate; the brightest parts of the image have a greater concen-

\* A review is given by James and Kornfeld, *Chem. Rev.*, **30**, 1 (1942).

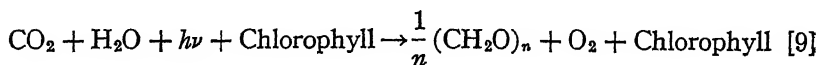
tration of quanta, and consequently more grains are reduced to silver. The unaffected grains are dissolved out with sodium thiosulfate ("hypo") and the plate is washed and dried. The bright parts of the image become the dark spots on the plate, and the plate is therefore called a negative.

In printing, the plate is placed over a paper coated with silver halide and exposed to the light. The dark spots of silver on the negative absorb the light, whereas the unaffected areas permit light to pass through and act on the silver halide, producing a negative of the first negative. This double reversal produces a print in which the dark and light parts agree with the dark and light parts of the original object.

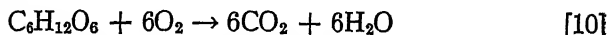
The silver halides respond only to the ultraviolet and to the shorter wavelengths of the visible spectrum, but by mixing in the emulsion certain red dyes, such as dicyanin, the plate becomes sensitive also to red. Such red-sensitive plates are called panchromatic plates and give much better tone values to colored objects. This phenomenon constitutes another example of photosensitization. The red light is less scattered than the blue, and much clearer pictures of distant objects through a hazy atmosphere are obtained with red-sensitive plates using a color filter which absorbs the blue. This method is used in aerial photography.

**Biological Applications of Photochemistry.** The most important photochemical reaction in the world is the union of carbon dioxide and water in plants through the agency of sunlight and chlorophyll. Chlorophyll is a complex organic compound containing magnesium, which gives to plants their green color. It absorbs red and blue and, to a lesser extent, green light. The activated chlorophyll thus formed is responsible for the production of the starting material for all plant growth, utilizing carbon dioxide and water.

The important primary reaction involved in the growth of plants may be represented by the equation



Now the reaction



evolves 672,000 cal. of heat, and the reverse reaction must absorb 672,000/6 or 112,000 cal. per gram atom of carbon. The energy of activation required for reaction (9) must be at least as great as the endothermic heat of reaction (page 372). This energy of 112,000 cal. per mole corresponds to a wavelength of about 2300 Å. or less.

Short ultraviolet light absorbed by carbon dioxide or water is known to bring about a reaction between carbon dioxide and water, but there is practically no radiation of this wavelength in the sun's radiation that reaches the surface of the earth.

Chlorophyll, however, acts as a photosensitizer, absorbing visible light and making it available for photosynthesis in the plant. But there is something unique about the reaction. Photons of red light correspond to only 40,000 cal. per mole and yet they are able to do chemical work which demands at least 112,000 cal. per mole. Obviously, nearly three or more photons must work together to bring about the reaction, but no reaction has yet been observed in the laboratory where low-energy photons can add together in a single step to do a high-energy job of this kind.

It is likely that reaction (9) takes place in several steps, each requiring one quantum, and each leading to a further partial reduction of the carbon dioxide. Experiments on algae show that the quantum yield under the most favorable condition is about 0.1 molecule of carbon dioxide consumed or oxygen evolved per quantum,\* corresponding to an efficiency with red light of about 28 per cent. Previously it had been erroneously thought that the quantum yield was 0.25 corresponding to a much higher efficiency. Recent experiments† with isotopic tracers (page 617) suggest that the carbon dioxide first adds on to a complex molecule which has a carboxyl group and a hydroxyl group, the unit having a molecular weight of about 1000. Some type of polymerization then gives rise to cellulose or related products.

Another photochemical reaction of biological importance is the production of vitamin D, which prevents rickets and brings about the normal deposition of calcium in growing bones. Steenbock found that rickets could be prevented by subjecting the food as well as the patient to ultraviolet light below 3100 Å. Later the provitamin was traced to ergosterol.

*Example 8.* When ergosterol is irradiated with ultraviolet light below 3100 Å. vitamin D, the antirachitic vitamin, is produced in proportion to the number of quanta absorbed. When irradiated ergosterol was included in a diet otherwise devoid of vitamin D, it was found that absorbed radiant energy of about 750 ergs was necessary to prevent rickets in a rat when fed over a period of two weeks. The light used had a wavelength of 2650 Å.

\* Manning, Stauffer, Duggar, and Daniels, *J. Am. Chem. Soc.*, **40**, 266 (1938).

† Ruben and Kamen, *J. Am. Chem. Soc.*, **62**, 3451 (1942).



(a) How many quanta are necessary to give 750 ergs?

$$\epsilon = h\nu = 6.62 \times 10^{-27} \times \frac{3.0 \times 10^{10}}{2.65 \times 10^{-5}} = 7.4 \times 10^{-12}$$

$$\text{Number of quanta} = \frac{750}{7.4 \times 10^{-12}} = 1.01 \times 10^{14}$$

(b) Assuming that the primary photo-process is the only chemical reaction, how many molecules of vitamin D per day are necessary to prevent rickets in a rat?

$$\text{Molecules per day} = \frac{1.01 \times 10^{14}}{14} = 7.25 \times 10^{12}$$

(c) If vitamin D has a molecular weight of the same order of magnitude as ergosterol (382) how many grams of vitamin D per day are necessary to prevent rickets in a rat?

$$\text{Grams per day} = \frac{7.25 \times 10^{12}}{6.02 \times 10^{23}} \times 382 = 4.6 \times 10^{-9}$$

The first measurements of this type were made before the vitamin D had been isolated. After the pure vitamin was isolated in nearly pure form it was found that  $5 \times 10^{-8}$  g. per day was the minimum dosage required to prevent rickets in a rat. This value is in agreement with the quantity estimated from theoretical photochemistry at a time when the nature of the vitamin was still unknown.

Müller and others have established the fact that mutations, leading to new species, can be produced in plants and insects by radiation with x rays. Apparently the cells which are responsible for hereditary influence cannot be affected by mechanical methods without injuring the cells, but occasionally they can be influenced without serious injury by a quantum of x rays. Collisions between quanta of x rays and effective parts of the cells are very rare and can be detected only by the extraordinary magnification occurring in the growth of an organism. It has been suggested that *some* of the naturally occurring mutations which are responsible for the spontaneous origin of species and biological evolution are produced by cosmic radiation and gamma rays from traces of radioactive material both of which are similar to x rays.

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## PROBLEMS

1. An energy of 24,700 cal. per mole corresponds to what wavelength?

*Ans.* 11,570Å.

2. (a) What is the energy per photon of violet light having a wavelength of 4000Å?

(b) How many calories per mole are there in 1 einstein ( $6.02 \times 10^{23}$  quanta) of this radiation? *Ans.* (a)  $4.97 \times 10^{-12}$  erg per quantum. (b) 71,450 cal.

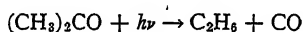
3. The following calculations are made on a uranyl oxalate actinometer, assuming that the energy of all wavelengths between 2540Å. and 4350Å. is completely absorbed. The actinometer contains 20 ml. of *M*/20 oxalic acid which also is *M*/100 with respect to uranyl sulfate. After 2 hours of exposure to ultraviolet light, the solution required 34 ml. of  $\text{KMnO}_4$  solution to titrate the undecomposed oxalic acid. The same volume, 20 ml., of unilluminated solution required 40 ml. of the  $\text{KMnO}_4$  solution. If the average energy of the quanta in this range may be taken as corresponding to a wavelength of 3500Å. how many ergs were absorbed per second in this experiment?

*Ans.* 124,000 ergs.

4. The photopolymerization of anthracene reaches a stationary state owing to the thermal decomposition of the dianthracene. For the photoreaction the temperature coefficient  $\tau$  is 1.1, and for the thermal reaction  $\tau$  is 2.8 where  $\tau$  is defined as  $k_{t+10}/k_t$ .

Calculate the effect of a 10° rise in temperature upon the amount of dianthracene formed when the photostationary state is reached. *Ans.* 60.7 per cent decrease.

5. A sample of gaseous acetone is irradiated with monochromatic light of a wavelength of 3130Å. Light of this wavelength decomposes the acetone according to the equation



The reaction cell used has a volume of 59 ml. The acetone vapor absorbs 91.5 per cent of the incident energy. During the experiment the following data are obtained:

Temperature of reaction	= 56.7°
Initial pressure	= 766.3 mm.
Final pressure	= 783.2 mm.
Time of radiation	= 7 hours
Incident energy	= 48,100 ergs per second

How many molecules are decomposed per quantum of absorbed energy, i.e., what is the quantum yield? *Ans.* 0.17 molecule per quantum.

6. According to the hypothesis of Franck, the molecules of the halogens dissociate into one normal atom and one excited atom. The wavelength of the convergence limit in the spectrum of iodine is 4995Å

(a) What is the energy of dissociation of iodine into one normal and one excited atom?

(b) The lowest excitation energy of the iodine atom is 0.94 volt. What is the energy corresponding to this excitation?

(c) Compute the heat of dissociation of the iodine molecule into two normal atoms, and compare it with the value obtained from thermochemical data, 34.5 kcal. per mole.

Ans. (a) 57.22. (b) 21.67. (c) 35.54 kcal.

7. (a) Calculate  $x$  in Table I. (b) Calculate  $y$  in Table I.

8. If a reaction responds to both red and violet light, 7000Å. and 4000Å. with an equal quantum efficiency will there be more photochemical reaction per 100 cal. of light in the red or in the blue? How much more?

9. How many calories of sunlight of average wavelength, 6000Å. will be required to synthesize a kilogram of carbohydrate material ( $\text{CH}_2\text{O}$ ) if 10 photons are required for every molecule of carbon dioxide utilized?

10. (a) How many calories per mole is equivalent in energy to 2 electron volts? A lead storage battery gives about 2 volts.

(b) How many calories per mole is equivalent to 100,000 volts? X rays have energies of about 100,000 volts.

(c) How many calories per mole is equivalent in energy to 20 million electron volts? Cosmic rays have energies of about 20 million electron volts.

11. The oxidation of rubrene ( $\text{C}_{42}\text{H}_{24}$ ) is effected by oxygen at a wavelength of 4360Å. with a quantum efficiency of 1 molecule per quantum. How many calories of this light will be required to photo-oxidize 1 g. of rubrene?

12. Ammonia is decomposed by ultraviolet light of 2000Å. with a quantum yield of 0.14 molecule per photon absorbed. (a) How many joules of this light would be necessary to decompose 1 g. of ammonia? (b) Offer a suggestion to explain this comparatively low quantum yield.

13. For 900 seconds light of 4360Å. was passed into a carbon tetrachloride solution containing bromine and cinnamic acid. The average energy absorbed was 19,190 ergs per second. Some of the bromine reacted to give cinnamic acid dibromide, and, in this experiment, the total bromine content decreased by  $3.83 \times 10^{19}$  molecules. (a) What was the quantum yield? (b) State whether or not a chain reaction was involved. (c) If a chain mechanism is involved, suggest suitable reactions which might explain the observed quantum yield.

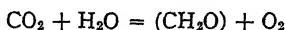
14. (a) What is the energy per quantum of ultraviolet light of 3663Å? (b) What is the energy of this light in calories per einstein?

15. If 3 per cent of the energy consumed by a certain lamp is converted into ultraviolet light having an average wavelength of 3000Å., how many kilowatt-hours will be required to produce a mole of material by means of a photochemical reaction in which one molecule is produced for each photon. Assume that all the ultraviolet light is absorbed by the reaction system.

16. Chloroform is often kept in dark bottles to prevent photo-oxidation by air, giving phosgene which is poisonous. The quantum yield of the photo-oxidation has been reported to be about 100 molecules per photon with light of 4360Å. How many grams of chloroform will be photo-oxidized by 10 cal. of this light?

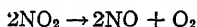
17. The quantum yield in the photodecomposition of hydriodic acid is 2. (a) Write the equation for the reaction. The reaction proceeds with light of 2820Å. and shorter wavelengths. (b) What statements can be made regarding the absorption spectrum and the energy of dissociation?

18. In the process of photosynthesis about 10 quanta of red light at  $6200\text{\AA}$ . are required for the reaction of one molecule of carbon dioxide with one molecule of water, according to the reaction



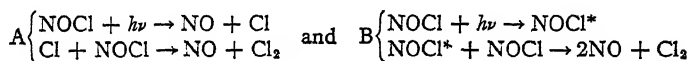
The heat of combustion of a carbohydrate ( $\text{CH}_2\text{O}$ ) evolves 112,000 cal. of heat per carbon atom. Calculate the energy efficiency of the process, i.e., the ratio of 112,000 to the number of calories of light absorbed per mole.

19. Nitrogen dioxide is decomposed photochemically by light of  $4050\text{\AA}$ . with a quantum yield of 0.5 molecule per photon, according to the reaction



The thermal reaction runs in the reverse direction. When an enclosed sample of nitrogen dioxide is illuminated for a long period of time the quantum yield decreases and approaches zero. Suggest a mechanism to explain these facts and write the chemical equations.

20. Two mechanisms have been proposed for the photochemical decomposition of NOCl:



What quantum yield would be expected for each mechanism? Given the following experimental facts, state which mechanism is probably correct:

The range of wavelengths effective in decomposition lies between  $3650$  and  $6400\text{\AA}$ .

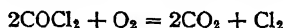
The substance NOCl possesses well-defined absorption bands above  $2500\text{\AA}$ . with no regions of continuous absorption.

The minimum dissociation energy required to give NO and Cl is  $46,400$  cal.

21. Explain the possibility of having quantum yields depend upon (a) pressure, (b) temperature, (c) concentration of non-reacting molecules, (d) wavelength of light.

22. The photochemical reaction between bromine and hydrogen to give HBr using light of  $5000\text{\AA}$ . has a quantum yield of zero below  $150^\circ$  and between 1 and 2 at higher temperatures. The quantum yield for the photochemical reaction between chlorine and hydrogen is about  $10^6$ . Explain the difference in the behavior of bromine and chlorine.

23. The photochemical oxidation of phosgene, sensitized by chlorine has been studied by Rollefson and Montgomery.\* The overall reaction is



and the rate expression which gives the effect of the several variables is

$$\frac{dc_{\text{CO}_2}}{dt} = \frac{kI_0c_{\text{COCl}_2}}{1 + k'c_{\text{Cl}_2}/c_{\text{O}_2}}$$

where  $I_0$  is the intensity of the light. The quantum yield is about two molecules per quantum. Devise a series of chemical equations involving the existence of the free radicals ClO and COCl which will give a mechanism consistent with the rate expression.

\* Rollefson and Montgomery, *J. Am. Chem. Soc.*, **55**, 142, 4025 (1932).

## CHAPTER XXI

### NUCLEAR STRUCTURE

The atom consists of a central nucleus of very small dimensions ( $10^{-12}$  cm. in diameter) in which is concentrated most of its mass, surrounded by electrons which give a total diameter of the order of  $10^{-8}$  cm. The nucleus itself is complex as shown by the natural radioactivity of the heaviest elements, the many different energy levels which are involved in the artificial disintegration of the elements, and the variety of nuclei which are known.

**Discovery of Radioactivity.** The first radioactive substance was discovered by Henri Becquerel in 1896. It had been shown by Roentgen, in the previous year, that the bombardment of the walls of a vacuum tube by a beam of electrons gives rise to a new type of rays, which, because of their puzzling characteristics, he called x rays. The portion of the tube where these rays originate was observed to fluoresce brilliantly, and it was assumed that this fluorescence might be connected with the new type of radiation.

Many substances were known to fluoresce under the stimulus of the sun's rays, and it was natural, in the light of Roentgen's discovery, that all substances which exhibit fluorescence should be subjected to careful examination. Among those who became interested in these phenomena was Becquerel. He studied the action of a number of fluorescent substances, among which was the double sulfate of potassium and uranium. This salt, after exposure to sunlight, was found to emit a radiation capable of affecting a carefully protected photographic plate. On checking with a proper control he found that preliminary stimulation by sunlight was unnecessary. Further investigation proved that the fluorescence had nothing to do with the photographic action, since both uranous and uranic salts were found to exert similar photographic action, notwithstanding the fact that uranous salts are not fluorescent. The activity of both uranous and uranic salts was found to be proportional to their content of uranium. The spontaneous emission of penetrating rays was called *radioactivity*.

A systematic examination of uranium and thorium minerals by Madame Curie led to the discovery that pitchblende, one of the principal ores of uranium, was considerably more radioactive than uranium

itself. She and her husband carried out the painstaking search for the unknown substance in pitchblende which in minute traces was responsible for the increased radioactivity of the ore. Associated with the bismuth in pitchblende, a very active substance was discovered, to which Madame Curie gave the name polonium in honor of her native land, Poland. In like manner, an extremely active substance was found associated with barium in the alkaline earth group. This substance was called radium because of its great radioactivity. Several tons of high-grade ore are required, however, to produce 1 g. of pure radium. The pure bromides of radium and barium are prepared together, and the two salts are then separated by a series of fractional crystallizations.

In 1910, Madame Curie succeeded in obtaining metallic radium. It is a metal possessing a silvery luster, which dissolves in water with energetic evolution of hydrogen and tarnishes rapidly in air with the formation of the nitride and oxide. Its atomic weight is 226.

**Natural Radioactivity.** The radiations emitted by the radioactive elements occurring naturally are of three kinds. The alpha particles have a mass equal to that of the helium atom and are shot out with a velocity about one-tenth that of light. They have a positive charge of two units and are deflected slightly in an electrostatic or magnetic field. They possess great ionizing power but relatively little penetrating power — only a few centimeters in air at atmospheric pressure. The beta rays consist of negatively charged particles moving with speeds varying from two-fifths to nine-tenths of the speed of light. Whereas the alpha particles emitted by a particular radioelement have a definite velocity, the corresponding beta-ray emission consists of a flight of particles having widely different speeds. The penetrating power of the beta rays is conditioned by the speed of the particles, those which move most rapidly possessing the greatest penetrating power. The ionizing action of the beta rays is much weaker than that of the alpha rays. They are greatly deflected by an electrostatic or magnetic field. The gamma rays are identical with x rays, except that they have shorter wavelengths varying from about  $1 \times 10^{-8}$  cm. for the rays of low penetrating power, to less than  $1 \times 10^{-10}$  cm. for the penetrating rays. Obviously, gamma rays cannot be deflected from a rectilinear path by either electric or magnetic fields. The relative penetrating power of the three rays are roughly in the order 1, 100, and 10,000 for the alpha, beta, and gamma rays.

When a current of air is passed through a solution of a radium salt a small volume of a very radioactive gas is obtained. With the help of an extremely sensitive microbalance it was found to have an atomic

weight of 222. This fact and the chemical inertness of the gas showed that it belonged to the group of rare gases of the zero group in the periodic table. It was given the name *radon*.

The following experiment showed that the alpha particle is an ion of helium moving at high velocity. A glass bulb was blown with walls thin enough to permit the passage of the alpha particles, but of sufficient strength to withstand atmospheric pressure. The bulb was filled with radium or radon, and then enclosed in an outer glass tube, to which a spectrum tube had been sealed. On exhausting the outer tube, and examining the spectrum of the residual gas, evidence of helium was obtained after a few days. In another experiment, the inner tube was filled with pure helium under pressure, while the exhausted outer tube was examined for helium. No trace of the gas could be detected spectroscopically, even after an interval of several days, thus proving that the helium detected in the first experiment must have resulted from the alpha particles which had been shot out from the radon with sufficient energy to penetrate the thin walls of the inner tube. These experiments leave no room for doubt that an alpha particle becomes a helium atom when it loses its velocity and its positive charge becomes neutralized.

There is an abundance of experimental evidence which proves that only one alpha particle is expelled from each atom of radium in the formation of radon. The process may be represented by the equation,



The atomic weight of radium is 226, and that of helium is 4; the atomic weight of radon is then nearly 222.

**Experimental Measurements.** Action on a photographic plate through opaque paper constitutes one of the simplest qualitative tests for the radioactivity of a substance. This method can be used to reveal the distribution of a radioactive substance within an object, such as a mineral or a leaf.

Some materials such as zinc sulfide become luminous when exposed to radiation from a radioactive material, and the intensity of this radioluminescence is roughly proportional to the radioactivity. When examined with a lens in a simple instrument called a spinthariscopes, the luminescence is seen to consist of a series of scintillations caused by the bombardment of alpha particles on the zinc sulfide. Practical use of this phenomenon is made in luminous paints, which are used, for example, on watch dials. A low-grade material of feeble radioactivity is mixed intimately with zinc sulfide and the resulting scintillations are so frequent as to produce a uniform glow to the unaided eye.

The best quantitative measure of radioactivity is obtained from

ionization. The radioactive material sends out radiations which ionize the surrounding gas and when an electrostatic field of the proper voltage is applied, the resulting current is a measure of the radioactivity. The current is measured by means of a delicate electroscope or electrometer, or may be amplified by a vacuum-tube circuit. The most sensitive instrument is the Geiger-Müller counter, which can detect individual ionizing particles. It consists of a wire in the center of a metal cylinder enclosed in a tube with a suitable gas. The wire is maintained at a potential several hundred volts positive to the cylinder, and the entrance of an ionizing particle produces a momentary flow of current, multiplied by ionic collisions, which is amplified and caused to operate a counting dial.

The Wilson cloud chamber provides important means for studying ionizing rays. The paths of individual alpha or beta particles or ejected electrons are rendered visible by shooting the particles into a chamber containing supersaturated water vapor. Each alpha particle produces about 100,000 gas ions and each of these ions condenses a droplet of water. The alpha particles travel in straight lines\* and leave behind them a wake of water droplets which is easily seen and photographed as shown in Fig. 154. The beta rays are more easily deflected

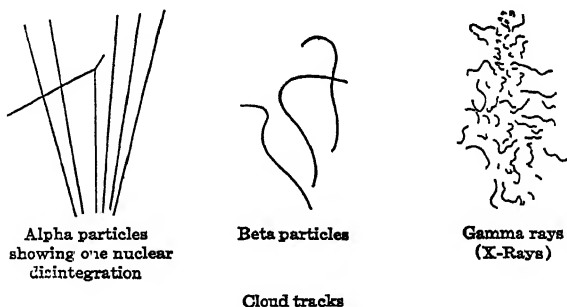


FIG. 154

and their paths are quite crooked. The gamma rays release a large number of secondary electrons from the molecules which they strike. The energy of these secondary electrons is lower and the paths are short and crooked.

**Disintegration of the Radioelements.** The disintegration of the radioelements involves changes in the nuclei of the atoms whereas ordinary chemical reactions involve changes only in the arrangement of atoms in molecules. The former have energies of the order of  $10^9$

\* Very rarely a direct collision with a nucleus occurs and the alpha particle is then deflected abruptly.



and more calories per mole and the latter changes of  $10^4$  to  $10^5$  calories per mole. Energies of a billion calories per mole have become available only recently with the discovery of radioactivity and the development of extremely high voltages. The energies involved in nuclear disintegrations are so great that the slight increases in energy produced by raising the temperature are entirely negligible, and as a result, no detectible change in the rate of radioactive disintegrations has been observed in studies extending from liquid air temperatures to  $1000^\circ$ .

On the average, a definite fraction of the atoms of a radioelement decomposes per unit of time and as a result of a nuclear transformation an alpha or a beta particle is expelled with great violence or a gamma ray is emitted. Other types of particles are sometimes emitted in disintegrations of elements which are rendered artificially radioactive.

Since the number of atoms disintegrating is proportional to  $n$ , the number of atoms present, the simple equation for the first-order reaction, page 345, applies with exactness and

$$\frac{-dn}{dt} = kn \quad [1]$$

where  $k$  is called the disintegration constant. Integrating equation (1)

$$-\ln n = kt + C \quad [2]$$

changing to exponentials and evaluating the constant  $C$ ,

$$n = n_0 e^{-kt} \quad [3]$$

where  $n_0$  is the number of atoms of the radioelement at  $t = 0$ .

The *half-life*,  $t_{1/2}$ , as explained on page 346, is

$$t_{1/2} = \frac{0.6932}{k} \quad [4]$$

The *average life* is the average life expectancy of the atoms present at any starting time. The atoms disintegrating,  $-dn$  in number, in the time interval  $dt$  at time  $t$  have had a life of length  $t$  from the starting time, i.e., the time when  $t$  is taken as zero. The average life is then

$$\begin{aligned} t_{\text{average}} &= \frac{1}{n_0} \int_0^\infty t(-dn) \\ &= \frac{1}{n_0} \int_0^\infty tkn \, dt \\ &= \int_0^\infty kte^{-kt} \, dt \\ &= \frac{1}{k} \end{aligned} \quad [5]$$

Thus the average life is the reciprocal of the radioactivity constant.

When one radioactive element disintegrates another may be formed, and the disintegration constant of the second radioelement is usually different from that of the first one. A series of consecutive unimolecular decompositions results which can be handled by the methods of differential equations, as illustrated on page 357. Radon is produced continuously by the disintegration of radium and radon, in turn, continuously decomposes into another radioelement, radium A. The rate at which radon is produced from a quantity of radium is given by the expression  $k_1 n_1$ , where  $n_1$  is the number of radium atoms, and  $k_1$  is the disintegration constant of radium or the fraction decomposing per unit of time; the rate at which it decomposes is given by the expression  $k_2 n_2$ , where  $n_2$  is the number of radon atoms and  $k_2$  is the disintegration constant of radon. When the rate of production of a radioelement from its parent element is equal to its rate of disintegration into the next succeeding element of the series, the substance is said to be in radioactive equilibrium. Under equilibrium conditions, radon is decomposing at the same rate that it is being formed and

$$k_1 n_1 = k_2 n_2 \quad [6]$$

Then at equilibrium

$$\frac{n_1}{n_2} = \frac{k_2}{k_1} = \frac{t_{1/2,1}}{t_{1/2,2}} \quad [7]$$

If the life of the parent element is long compared with the life of the disintegration products and if sufficient time is allowed for equilibrium to be attained, the ratio of the quantities of successive radioelements is the same as the ratio of their half-lives. It is evident that the short-lived elements cannot accumulate in large quantities, but because of their rapid disintegration they may contribute largely to the radioactivity of the total material.

*Example 1.* For the radio disintegration of radium,  $t_{1/2} = 1590$  years and for radon  $t_{1/2} = 3.82$  days. How many milliliters of radon at  $25^\circ$  and 1 atm. are in equilibrium with 1 g. of radium?

$$1 \text{ g. radium} = 1/226 = 0.00442 \text{ gram-atom}$$

$$\frac{n_{\text{Ra}}}{n_{\text{Rn}}} = \frac{t_{1/2, \text{Ra}}}{t_{1/2, \text{Rn}}} = \frac{0.00442}{n_{\text{Rn}}} = \frac{1590 \times 365.25}{3.82}$$

$$n_{\text{Rn}} = 2.87 \times 10^{-8} \text{ gram-atom}$$

$$\text{Vol. radon} = 2.87 \times 10^{-8} \times 22,412 \times \frac{298.1}{273.1} = 7.06 \times 10^{-4} \text{ ml.}$$

When a short-lived radioelement is removed from its long-lived parent element a new supply is regenerated, rapidly at first and then more slowly as the rate of decay of the accumulating element approaches the rate of its formation. A sample of radium in equilibrium with its disintegration products contains a short-lived product which gives intense gamma rays. When the radon is pumped off or swept out with

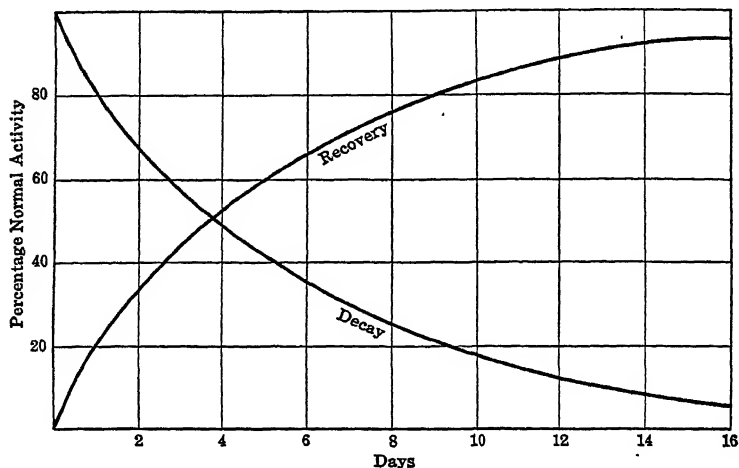


FIG. 155

a current of air the radium loses its gamma-ray activity but regains it as the disintegration products are produced again from the radium. The rate of recovery of the gamma ray in radium and its disintegration products is the same as the rate of gamma-ray decay of the radon and its disintegration products. These facts are shown by the curves of Fig. 155 and by equations (8) and (9).

$$I = I_0 e^{-kt} \quad (\text{decay}) \quad [8]$$

$$I' = I_0' (1 - e^{-kt}) \quad (\text{recovery}) \quad [9]$$

where  $I_0$  is the intensity of radioactivity at the beginning of the experiment and  $I$  is the intensity of the radon after time  $t$  after the separation and  $I'$  is the corresponding value for the radium.

**The Radioelements and the Periodic Table.** If a negatively charged wire is introduced into a vessel containing radon, an extremely radioactive substance, known as the "active deposit," is condensed upon its surface. This deposit, which can be detected by neither balance nor microscope, has been found to consist of the successive disintegration products of radon. The atomic disintegration of radon takes place

in eight distinct successive stages, the first four radioelements of the active deposit being characterized by very short average lives, ranging from 38.5 minutes for RaB, to  $2 \times 10^{-4}$  second for RaC', whereas the remaining elements of the series undergo transformation at a much

## DISINTEGRATION SERIES OF THE RADIOELEMENTS

Name	Group	At. Weight	At. Number	Name	Group	At. Weight	At. Number	Name	Group	At. Weight	At. Number
Uranium I $4.5 \times 10^9$ years	VI <sub>A</sub>	(238)	92	Actinouranium $7.1 \times 10^8$ years	VI <sub>A</sub>	(230)	92	Thorium $1.39 \times 10^{10}$ years	IV <sub>A</sub>	(232)	90
Uranium X <sub>1</sub> 24 5 days	IV <sub>A</sub>	(234)	90	Uranium Y 24 6 hours	IV <sub>A</sub>	(231)	90	Mesothorium I 6 7 years	II <sub>A</sub>	(228)	88
Uranium X <sub>2</sub> 1.14 minutes	IV <sub>A</sub>	(234)	91	Protactinium $3.2 \times 10^4$ years	V <sub>A</sub>	(231)	91	Mesothorium II 0.13 hours	III <sub>A</sub>	(228)	89
Uranium II $2.7 \times 10^5$ years	VI <sub>A</sub>	(238)	92	Radioactinium 18 9 days	IV <sub>B</sub>	(227)	90	Radiothorium 1 90 years	IV <sub>A</sub>	(228)	90
Ionium $5.2 \times 10^4$ years	IV <sub>A</sub>	(230)	90	Actinium X 11 2 days	II <sub>A</sub>	(228)	88	Thorium X 5 64 days	II <sub>A</sub>	(224)	88
Radium 1590 years	II <sub>A</sub>	(226)	88	Actinium 3.0 seconds	0	(210)	86	Thorium 54 5 seconds	0	(220)	86
Radon 3.82 days	0	(222)	86	Actinium A $2 \times 10^{-7}$ seconds	VI <sub>B</sub>	(210)	84	Thorium A 0 16 second	VI <sub>B</sub>	(210)	84
Radium A 3.0 minutes	VI <sub>B</sub>	(218)	84	Actinium B 38 0 minutes	IV <sub>B</sub>	(211)	82	Thorium B 10 0 hours	IV <sub>B</sub>	(210)	82
Radium B 26 8 minutes	IV <sub>B</sub>	(214)	82	Actinium C 2.16 minutes	V <sub>B</sub>	(211)	83	Thorium C 60.5 minutes	V <sub>B</sub>	(212)	83
Radium C 19.7 minutes	V <sub>B</sub>	(214)	83	Actinium C' $5 \times 10^{-5}$ second	VI <sub>B</sub>	(211)	84	Thorium C' $3 \times 10^{-7}$ second	VI <sub>B</sub>	(212)	84
Radium C' $2 \times 10^{-4}$ second	VI <sub>B</sub>	(214)	84	Actinium D (End)	IV <sub>B</sub>	(207)	82	Thorium C'' 3.2 minutes	III <sub>B</sub>	(208)	81
Radium D 22 years	IV <sub>B</sub>	(210)	82					Thorium D (End)	IV <sub>B</sub>	(206)	82
Radium E 5.0 days	V <sub>B</sub>	(210)	83								
Radium F (Polonium) 140 days	VI <sub>B</sub>	(210)	84								
Radium G (Lead) (End)	IV <sub>B</sub>	(206)	82								

FIG. 156

slower rate, their average lives varying from 7.2 days to 32 years. Thorium and actinouranium disintegrate in a manner similar to that of uranium, giving rise to series of radioelements which, in general, are shorter lived than the members of the uranium series. The three disintegration series are given in Fig. 156.

The numbers within the circles denote the atomic weights of the elements; the small circles and dots at the right of the larger circles indicate the character of the radiation given out at each stage of the disintegration process. The half-life,  $0.693/k$ , of each element in the series is given below the name of the element. The roman numerals refer to the groups in the periodic table (page 7).

Fajans and Soddy, in 1913, pointed out that the expulsion of an alpha particle causes a radioactive element to shift its position in the periodic table two places in the direction of decreasing atomic weight, whereas the emission of a beta particle causes a shift of one place in the opposite direction.

The loss of an alpha particle, or helium atom, involves a loss of 4 units in atomic weight and of 2 units of positive electricity from the nucleus of the atom. In consequence of this loss, the atomic number defined on page 627 is diminished by 2 units, and the resulting new element finds a place in the periodic table two groups to the left of that occupied by the parent element. On the contrary, while the expulsion of a beta particle, or electron, involves practically no change in mass, the nucleus of the parent atom suffers a loss of 1 unit of negative electricity. This loss is equivalent to a gain of 1 unit of positive electricity,

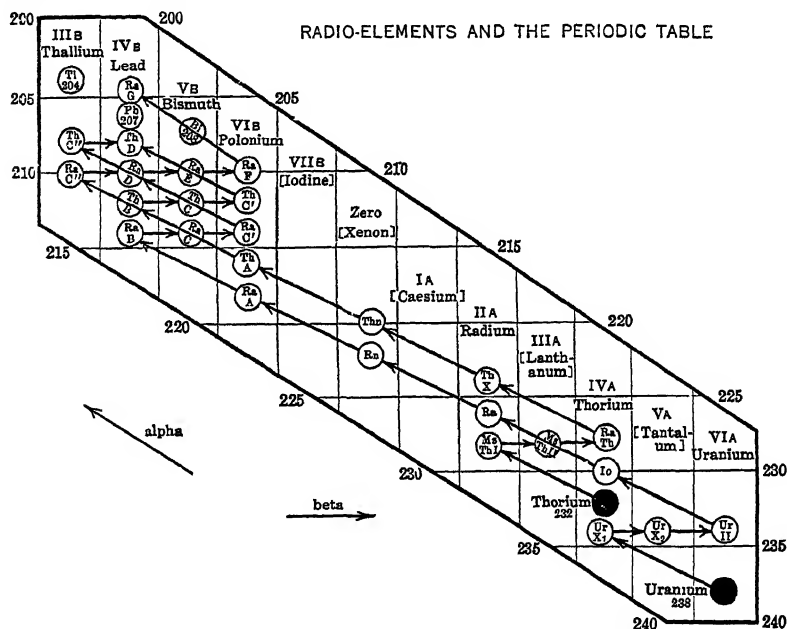


FIG. 157

or to an increase of 1 unit in the atomic number, and in consequence, the position of the new element in the periodic table is shifted one group to the right of that occupied by the parent element, with a corresponding increase in valence.

Soddy's arrangement of all the radioelements of the uranium and thorium series in accordance with this generalization is shown in Fig. 157. Thus, starting with the element uranium in group VIA, we may follow the successive steps in the radium disintegration series which were depicted in Fig. 156.

Perhaps the most striking feature of the table is the occurrence of several elements of different atomic weights in the same place, as for

example in group IVB, where in the place occupied by the element Pb, we also find RaB, RaD, ThB (and AcB\*), together with four other elements which are stable end products. These individual members of such a group having different atomic weights but the same position in the periodic table are called *isotopes*.

**Avogadro's Constant from Radioactivity Data.** Since it has been proved that each alpha particle is transformed into a helium atom, and since we can count the alpha particles and measure the volume of helium, we have at once a direct method for determining the number of molecules in a gram-molecule of helium, and this number is called the *Avogadro number*.

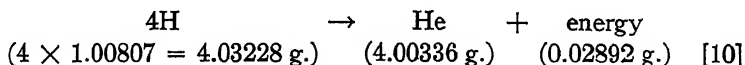
*Example 2.* Rutherford and Geiger found that radium emits  $3.4 \times 10^{10}$  alpha particles per gram per second. Rutherford and Boltwood found that radium produces helium at the rate of  $1.07 \times 10^{-4}$  ml. per gram per day, measured under standard conditions. Calculate the Avogadro number.

$$\frac{22,400}{1.07 \times 10^{-4}} \times 3.4 \times 10^{10} \times 24 \times 60 \times 60 = 6.15 \times 10^{23}$$

This value is in good agreement with others obtained by entirely different methods.

From the number of alpha particles and the total electrical charge carried it has been found that each alpha particle has a charge of  $9.3 \times 10^{-10}$  electrostatic unit. Deflection in an electrostatic field was in the direction which showed that the charge was positive. Since the fundamental unit of electricity (the charge on the electron) is  $4.80 \times 10^{-10}$  electrostatic unit (page 657), it follows that the alpha particle carries two positive charges.

**The Packing Effect.** The mass of the helium atom is nearly but not quite equal to the mass sum of four hydrogen atoms. There is now abundant evidence that the nuclei of all the elements are composed of units having approximately the mass of the hydrogen ion or proton, as suggested by Prout in 1815. The discrepancy in mass in the case of helium is shown by the equation



according to which there is the disappearance of 0.02892 g. of material and at the same time there is the production of an equivalent amount of energy.

\* A disintegration product of actinouranium not shown in Fig. 157.

According to the theory of relativity, mass and energy are interconvertible and are related by the equation

$$1 \text{ g.} = 8.988 \times 10^{20} \text{ ergs} \quad [11]$$

The factor  $8.988 \times 10^{20}$  is the square of the velocity of light, all quantities being expressed in the centimeter-gram-second system of units. The loss of weight of 0.029 g. is offset by the evolution of  $0.029 \times 9 \times 10^{20}$  ergs, or  $5.8 \times 10^{11}$  cal. of energy per mole. This energy is far greater than any energy available from ordinary chemical reactions.

This apparent loss of mass is called the packing effect and the *packing fraction* is defined as the difference between the actual mass of the isotope and the nearest whole number divided by this mass number. Thus the mass of one of the chlorine isotopes is 34.983 and the packing fraction is  $\frac{34.983 - 35.000}{35.000} = -0.00048$ . Packing fractions are usually

expressed in parts per 10,000 and so the packing fraction of chlorine is written  $-4.8$ . Since oxygen is taken as the standard, elements with positive packing fractions are less stable than oxygen, those with negative packing fractions are more stable. The elements in the middle range of the periodic table seem to be the most stable, the light elements and the heavy elements possessing positive packing fractions.

**Nuclear Units.** For several years it was thought that positive protons and negative electrons and helium nuclei or alpha particles were the units from which all atoms are built.

In 1932, the *positron* was discovered by Anderson, during an examination in a cloud chamber of particles emitted during the bombardment of a gas by cosmic rays. A powerful magnetic field of known strength was placed across the chamber and cloud tracks were obtained with such a large curvature that the particle producing the track could have a mass only of 0.00054 on the atomic weight scale, i.e., the mass of an electron. But the curvature was in the wrong direction. In previous experiments, there was no way of telling in which of the two directions along the cloud track the particle was traveling. In this particular experiment the particle passed through a thin lead sheet and a photograph was taken at right angles to the sheet. It showed the curvature of the path on one side to be greater than that on the other and hence the particle was traveling through the lead in the direction pointing to the greater deflection (lower velocity). The observed curvature in the magnetic field could be explained only on the assumption that the particle was charged *positively*. Since this discovery there has been abundant proof of the frequent occurrence of these positively charged "electrons" or positrons.

In the same year the *neutron* was discovered by Chadwick. Previous investigators had bombarded light elements with alpha particles and obtained ionization effects at great distances. The nature of these penetrating radiations was in doubt. Chadwick bombarded beryllium with alpha particles and showed by the great penetration, by the failure to produce cloud tracks, and by the failure to be deflected in a magnetic field that the effects were produced by an uncharged particle having the mass of the hydrogen atom. This unit, called the neutron, had been predicted by Rutherford and by Harkins.

Also in 1932, Urey discovered the heavy isotope of hydrogen  $H^2$  or *deuterium*. The nucleus of this atom has a mass of 2 and one positive charge.

Our building blocks of all matter then are given in Table I.

TABLE I  
PRIMARY UNITS

Unit	Symbol	Mass	Charge
Proton	$p$	1.007589	+
Electron	$e, \beta^-$	0.000542	-
Neutron	$n$	1.00895	0
Positron	$e^+, \beta^+$	0.000542	+
Deuteron	$d$	2.014726	+
Alpha particle	$\alpha$	4.003842	2+

The mass of the hydrogen atom is  $1.007589 + 0.000542 = 1.00813$ .

It is now believed that the nuclei of atoms of all the elements are composed of protons and neutrons. Although electrons and positrons are given off when certain atomic nuclei disintegrate they do not necessarily exist in the nuclei as separate entities. In building up the elements of the periodic table, protons and neutrons are added together but whenever two protons and two neutrons are contained in the same nucleus the four units are believed to combine to give the nucleus of the helium atom, or an alpha particle. Thus the nucleus of hydrogen with a mass of 1 is a proton whereas the nucleus of deuterium with a mass 2 probably consists of a proton and a neutron. Lithium with a mass of 6 may consist of a helium nucleus (4) with a neutron and a proton, while  $Li^7$  may have added to this nucleus one more neutron. The nucleus of carbon of mass 12 may contain three helium nuclei, while  $C^{13}$  has three helium nuclei plus one neutron. By adjusting helium nuclei, protons, and neutrons the correct masses and the atomic



numbers (page 633) can be obtained, but these units may well lose their identities inside the nucleus. In the neutral atom the positively charged nucleus is surrounded by negative electrons.

**Transmutation.** We have seen that the heaviest elements undergo radioactive disintegration spontaneously, and it is possible to disintegrate the light elements artificially. Rutherford and Chadwick in 1921 successfully disintegrated nitrogen atoms by bombardment with alpha particles. The alpha particles have a definite range in nitrogen of about 7 cm., but some flashes of light, apparently due to the impact of fast-moving particles, could be detected on a sensitive screen at much greater distances. Deflections in a magnetic field indicated that the particles which caused these scintillations were protons. It might be expected that, if an alpha particle hits a hydrogen atom squarely, the hydrogen atom with a mass one-fourth as great could travel considerably farther — up to 28 cm. As a matter of fact, in pure nitrogen, flashes were detected up to a distance of 40 cm. Such a great range was explained on the hypothesis that the nucleus of the nitrogen atom is actually altered by the collision with the alpha particle and intra-atomic energy is released which drives the proton out with great additional force. Several other light elements such as boron and fluorine were disintegrated in the same way.

The study of the atomic nucleus received a great impetus when projectiles other than alpha particles were used for bombardment. Protons or deuterons, traveling at enormous velocities under potentials of a million volts and more, are very effective. Two principal types of apparatus are used for the acceleration. In the cyclotron,\* the ions are subjected to a moderately high voltage and guided around a spiral path by a powerful magnetic field. The voltage is altered at just the right frequency so that the ions (protons, deuterons, or helium nuclei) are accelerated each time they make one half-circle, and the applied voltage is thus cumulative. As the projectiles attain higher and higher voltages they move in circles of increasing radius, and when they reach the outer edge of the apparatus they are deflected by an electric field against a target of the material which is to be bombarded. In the electrostatic generator,† a rapidly moving belt carries electricity from charged points to a cylindrical or spherical electrode until a very high steady voltage is reached. The difficulties of insulation have been solved by placing the whole apparatus in a large steel tank containing air at several atmospheres pressure to increase the sparking

\* Lawrence and Livingston, *Phys. Rev.*, **40**, 19 (1932).

† Van de Graff, Compton, and van Atta, *Phys. Rev.*, **43**, 149 (1933).

potential.\* A series of metal hoops is arranged to give a gradual change of potential along an evacuated tube, within which the ions are accelerated.

The cyclotron gives deuterons with energies up to 16 million electron volts. Extremely high energies are necessary for the penetration of the electrostatic fields of the heavier nuclei by charged particles, and the cyclotron is thus most effective in producing transmutations in large quantity. The electrostatic generator gives energies up to 4 million volts, and is especially useful for making bombardments at definite and controlled voltages.

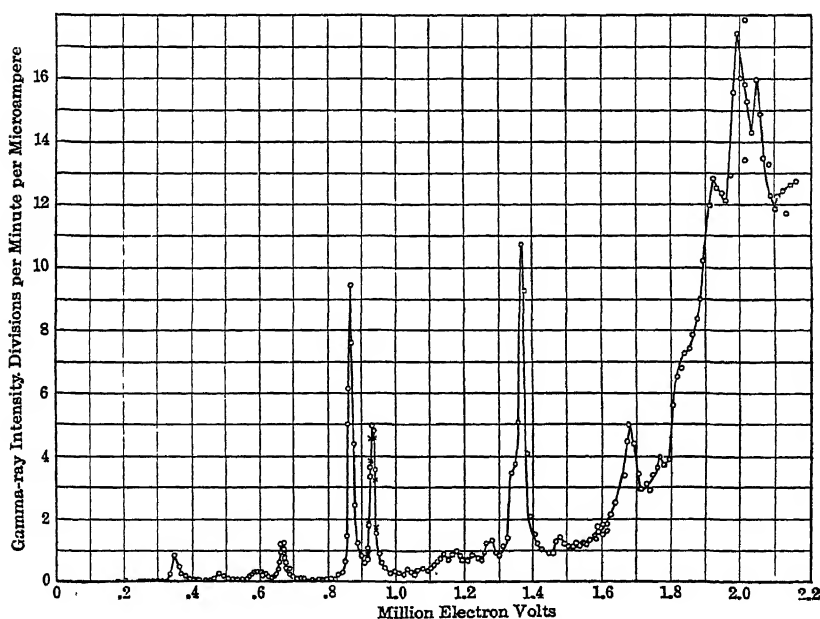


FIG. 158

In **Fig. 158** the intensity of gamma-ray radiation is plotted against voltage when the nuclei of fluorine atoms are bombarded with protons.† Calcium is not transmuted by protons at these voltages and so calcium fluoride is used as the target. The peaks in the voltage-excitation curve correspond to stable energy levels in the nucleus. Their resemblance to the peaks in the ionization potential curves of atoms shown on page 562 is evident. Energy changes in the outer part of an atom

\* Herb, Parkinson, and Kerst, *Phys. Rev.*, **51**, 76 (1937).

† Bernet, Herb, and Parkinson, *Phys. Rev.*, **54**, 398 (1938).

involve a few volts, whereas energy changes in the nucleus of an atom involve millions of volts.

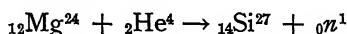
Cosmic rays and gamma rays of very high energy from nuclear reactions are also able to transmute elements.

The neutron has been found particularly effective in producing nuclear changes. Since it has no charge, it has no difficulty in reaching even highly charged nuclei. Neutrons may be produced by mixing an alpha-emitting substance, such as radium or radon, with beryllium powder, or in much larger quantities by bombarding beryllium or lithium targets with a beam of fast deuterons from a cyclotron or electrostatic generator.

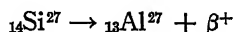
The concentration of radioactive elements may be facilitated if the nuclear reaction produces also a chemical reaction which permits a separation from the original material. For example, when a bottle of butyl bromide is exposed to neutrons the bromine atoms which are rendered radioactive are released from their organic linkages and can be extracted with water containing a little alkali. In this way the ratio of radioactive to normal bromide is greatly increased in the aqueous solution.

**Artificial Radioactivity.** In 1932, Irene Curie, daughter of the discoverers of radium, with her husband, F. Joliot, discovered that ordinary light elements can be made radioactive. They bombarded boron and aluminum and other light elements with alpha particles and obtained an emission of positrons which continued after the excitation by the alpha particles had ceased.

With magnesium the reaction is



The silicon produced from the magnesium is radioactive with a half-life of 4 seconds and gives off positrons, leaving a stable isotope of aluminum according to the reaction



In writing nuclear reactions it is necessary to balance them with respect to mass and with respect to charge. In other words, the sum of the superscripts (mass weights) on the left must be equal to the sum of the superscripts on the right; and the sum of the subscripts (atomic numbers) on both sides must be equal also.

Within ten years of the discovery of artificially induced radioactivity over 400 radioactive isotopes have been reported in the literature. In addition, over 140 stable isotopes are known, giving well over 500 isotopes distributed among the 92 chemically different elements. A few typical artificially produced radioactive isotopes are

listed in Table II together with their periods of half-life and the type of decay which they undergo. For more details and additional examples the list collected by Seaborg\* should be consulted. This table includes examples of several different types of radio-disintegration with half-life periods ranging from 0.02 sec. to more than 1000 years.

TABLE II  
TYPICAL RADIOACTIVE NUCLEI PRODUCED ARTIFICIALLY

Symbol	Half-Life	Nature of Decay
${}^3_1\text{H}$	~30 years	$\beta^-$
${}^{12}_5\text{B}$	0.022 sec.	$\beta^-$
${}^{12}_6\text{C}$	21.0 min.	$\beta^+$
${}^{14}_6\text{C}$	>1000 years	$\beta^-$
${}^{24}_{11}\text{Na}$	14.8 hours	$\beta^-, \gamma$
${}^{32}_{15}\text{P}$	14.1 days	$\beta^-$
${}^{59}_{26}\text{Fe}$	42 days	$\beta^-, \gamma$
${}^{57}_{27}\text{Co}$	270 days	$\beta^+; K\text{-capture}, \gamma$
${}^{64}_{29}\text{Cu}$	12.8 hours	$\beta^-; \beta^+; K\text{-capture}$
${}^{80}_{46}\text{Br}$	4.4 hours	$\gamma$ (Isomeric transition)
${}^{80}_{35}\text{Br}$	18 min.	$\beta^-, \gamma$
${}^{115}_{43}\text{Ma}$	62 days	$K\text{-capture}, \gamma$
${}^{115}_{49}\text{In}$	4.1 hours	$\gamma$ (Isomeric transition)
${}^{131}_{53}\text{I}$	8.0 days	$\beta^-, \gamma$
${}^{211}_{85}\text{Bi}$	7.5 hours	$K\text{-capture}; \alpha$
${}^{239}_{93}\text{Np}$	2.3 days	$\beta^-, \gamma$

Most artificial radioelements emit electrons ( $\beta^-$ ) or positrons ( $\beta^+$ ), but other types of decay also occur. In some cases a given isotope may undergo disintegration by one of two or even three different processes; these are separated by semicolons in the table as, for example in the case of  ${}^{57}_{27}\text{Co}$  and  ${}^{64}_{29}\text{Cu}$ .

Several isotopes listed illustrate the process known as *K-electron capture*, in which an external electron from the shell nearest the nucleus (the *K* shell defined on page 637) enters the nucleus, causing the atomic number to decrease by one unit. The filling of the vacancy in the *K* shell by other electrons causes the emission of x rays from the atom.

Frequently the emission of a particle, capture of an electron, or other nuclear process leaves a nucleus in an unstable condition, and it acquires a state of greater stability by the immediate emission of one or more gamma rays. Occasionally, however, such a higher-energy state may be metastable, which leads to the existence of *nuclear isomers* or *isobaric isotopes*, i.e., different isotopes having the same atomic weight

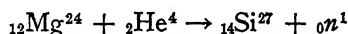
\* Seaborg, "Artificial Radioactivity," *Chem. Rev.*, **27**, 199 (1940).

as well as the same atomic number. For example, the bromine isotope  $^{80}_{35}\text{Br}$  characterized by a half-life of 4.4 hours emits gamma radiation without loss of either mass or charge, the *isomeric transition* resulting in the isotope having a half-life of 18 minutes.

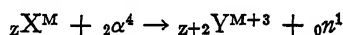
Frequently associated with gamma radiation are so-called *conversion electrons*. A gamma ray from the nucleus interacts with an outer electron and expels it with high speed. Such a process leaves the atom in an excited state of high-energy content, which often results in chemical reactivity. In such cases as  $^{80}_{35}\text{Br}$ , where the product is radioactive, its chemical nature may be traced by its radioactivity.

In Table II are also shown three isotopes of elements which have never been conclusively demonstrated in nature, elements 43 (Massium), 85, and 93.

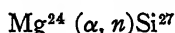
**Nuclear Reactions.** The processes by which radioelements are produced fall into a few general types. The reaction given on page 614,



is an example of the type reaction



A simplified notation for the same reaction is



where the first symbol in the parentheses is the bombarding particle, and the second is the emitted particle. A few examples of nuclear reactions are given in Table III, and a summary of the principal types is given in Table IV. In general, the efficiency of a reaction increases with the speed of the bombarding projectile. With the  $(n, \gamma)$  reaction, however, this is not true. Neutrons which have passed through a hydrogen-containing substance and hence have been slowed down by numerous collisions with hydrogen nuclei are much more easily captured by other nuclei. Such neutrons are called *thermal neutrons* because their velocities are about equal to the kinetic motions of the hydrogen atoms.

A more nearly complete summary of the principal reactions is given in abbreviated form in Table IV.

**Uses of Radioactivity.** Many uses had been developed for the naturally occurring radioactive elements (from lead to uranium in the periodic table) but the new, artificially produced radioactivity has greatly increased the interest in this work because radioactive forms of almost any element can now be obtained.

The medical uses of radioactivity are well known. Although serious

burns can be produced by radium, it is possible under properly controlled conditions to destroy early cancerous tissue and other abnormal growths without serious injury to the normal flesh. For such purposes radon is used. It is collected by bubbling air through a solution of a radium salt and by condensing out the radon at low temperatures in

TABLE III  
TYPICAL NUCLEAR REACTIONS

General Reactions	Example	Notation
${}_Z\text{X}^M + {}_0n^1 \rightarrow {}_Z\text{Y}^{M+1} + {}_0\gamma^0$	${}_{25}\text{Mn}^{55} + {}_0n^1 \rightarrow {}_{25}\text{Mn}^{56} + {}_0\gamma^0$	$\text{Mn}^{55}(n, \gamma)\text{Mn}^{56}$
${}_Z\text{X}^M + {}_1p^1 \rightarrow {}_{Z+1}\text{Y}^M + {}_0n^1$	${}_3\text{Li}^7 + {}_1p^1 \rightarrow {}_4\text{Be}^7 + {}_0n^1$	$\text{Li}^7(p, n)\text{Be}^7$
${}_Z\text{X}^M + {}_2\alpha^4 \rightarrow {}_{Z+2}\text{Y}^{M+3} + {}_1p^1$	${}_{20}\text{Ca}^{43} + {}_2\alpha^4 \rightarrow {}_{22}\text{Sc}^{46} + {}_1p^1$	$\text{Ca}^{43}(\alpha, p)\text{Sc}^{46}$
${}_Z\text{X}^M + {}_1d^2 \rightarrow {}_{Z+1}\text{Y}^M + {}_2n^1$	${}_{52}\text{Te}^{130} + {}_1d^2 \rightarrow {}_{53}\text{I}^{130} + {}_2n^1$	$\text{Te}^{130}(d, 2n)\text{I}^{130}$
${}_Z\text{X}^M + {}_0n^1 \rightarrow {}_{Z-2}\text{Y}^{M-3} + {}_2\alpha^4$	${}_{27}\text{Co}^{59} + {}_0n^1 \rightarrow {}_{25}\text{Mn}^{56} + {}_2\alpha^4$	$\text{Co}^{59}(n, \alpha)\text{Mn}^{56}$

very small glass tubes which are then sealed off. Radioactive sodium, as well as phosphorus, strontium, and iodine, offer promise of important therapeutic uses. They have a comparatively short life and leave no poisonous metals or continuing radioactivity in the body.

Several applications of radioactivity have been made to geology.\* One of the earliest was the determination of the age of the earth. The rates of radio-disintegration are well established and the age of a

TABLE IV  
PRINCIPAL NUCLEAR REACTIONS

Neutron Reactions	Deuteron Reactions	Proton Reactions	Alpha Reactions	Photonuclear Reactions
$n, \gamma$	$d, p$	$p, n$	$\alpha, n$	$\gamma, n$
$n, 2n$	$d, n$	$p, \gamma$	$\alpha, p$	
$n, p$	$d, \alpha$	$p, \alpha$		
$n, \alpha$	$d, 2n$			

given uranium or other radioactive mineral is obtained by simply dividing the amount of disintegration product by the rate at which the product is generated. If the life of the parent element is very long, the calculations are simplified. The amount of lead found in a uranium mineral is a measure of the amount of uranium which has undergone radioactive disintegration, provided that no lead has been brought from other places and none has been leached out. A determination of the atomic weight or a measurement of the relative distribution of

\* Goodman, "Geological Applications of Nuclear Physics," *J. Applied Physics*, **13**, 276 (1942)

isotopes can be used to correct for any ordinary lead present which did not come from the uranium or thorium in the sample of mineral. The accumulation of helium from alpha particles is used also for dating minerals. The earth must be at least as old as the oldest mineral which is found, and several have been established to be about a billion years old.

*Example 3.* A sample of pitchblende was found to contain 51.16 per cent uranium and 2.492 per cent lead, giving a lead-uranium ratio of 0.0486.\* An atomic weight determination showed that whereas most of the lead came from uranium and had an atomic weight of 206, some ordinary lead was present, requiring a correction of Pb/U to 0.0453. The disintegration constant for uranium is  $1.52 \times 10^{-10} \text{ year}^{-1}$ . How old must this mineral have been in order to accumulate this much lead?

$$\text{Ratio } \frac{U_{\text{disintegrated}}}{U_{\text{unchanged}}} = 0.0453 \times \frac{\text{At. wt. U}}{\text{At. wt. Pb}} = 0.0453 \times \frac{238}{206} = 0.0525$$

$$\frac{-dc}{dt} = kc$$

$$\frac{-0.0525}{dt} = 1.52 \times 10^{-10} \times 1$$

$$dt = 300 \text{ million years}$$

This is an approximate calculation assuming that for this problem 300 million years are infinitesimal! A more exact calculation may be made readily, thus

$$1.52 \times 10^{-10} = \frac{2.303}{t} \log \frac{1.000}{1.000 - 0.0525}$$

The use of radio-indicators offers a solution for certain analytical problems. The test for radioactivity is so much more sensitive than other physical or chemical tests that the minutest amount of material can be detected. The solubility of a difficultly soluble lead salt may be determined by placing a trace of radio-lead in a saturated solution and allowing the radio-lead to distribute itself between the solution and the solid. The distribution ratio can be easily and accurately determined by measuring the intensity of radioactivity. Again, it is possible with radio-indicators to determine the actual number of atoms of lead or other elements exposed in a crystal and accordingly the absolute surface can be calculated.

There has been uncertainty regarding two or three of the elements in the periodic table and a sufficient supply for tests was not available. These have now been produced in radioactive form and their properties have been studied.

The use of radioactive elements to give "tagged" atoms is furnishing an important means for studying the mechanism of certain chemical reactions and biological processes. For example, radioactive iodine and bromine have been used to follow the course of the halogen in organic reactions and radioactive manganese has been used to show that there is no interchange of manganese between the ions of different valence, as for example, between  $\text{MnO}_4^-$  and  $\text{Mn}^{++}$ , but that there is a rapid exchange between manganous ion and manganic oxalate ion.\*

By feeding radioactive phosphorus to a colony of rats and determining the radioactivity of the bone ash at frequent intervals, Hevesy found that a given atom of phosphorus remains in the bones only about a month, a fact which proved the hypothesis that the bones of a living animal are in a state of dynamic equilibrium with their surroundings. Radioactive phosphorus has been used also to determine the time required for inorganic phosphorus in the food to be converted into organic phosphorus material in the blood of rats.

Radioactive carbon,  $^{14}\text{C}$ , has been used effectively in studying biochemical reactions. Certain organisms, which give off carbon dioxide in respiration, are found to exchange carbon for the "tagged" radioactive carbon in carbon dioxide placed around them. Growing algae take up "tagged" carbon from dioxide and the radioactivity is found first in a material which contains a carboxyl group and has a molecular weight of about 1000. This appears to be one of the first stages in photosynthesis.†

Among the recent developments in physiology are the use of radioactive iron in the study of hemoglobin in the blood and the use of radioactive iodine in the study of goiter.

**Nuclear Fission and Intra-Atomic Energy.‡** When a uranium, thorium, or protoactinium nucleus is struck by a neutron it breaks down into two smaller nuclei, which are usually radioactive. Over fifty radioactive fission products are known, distributed among about twenty elements in the middle of the periodic table. Fast neutrons are required in most cases, but thermal neutrons are effective for the  $\text{U}^{235}$  isotope. The energy evolved in the process is enormous—of the order of 200 million electron-volts or nearly  $5 \times 10^{11}$  cal. per mole. In addition it is believed that several neutrons are emitted in each fission. Hence the possibility of a branched chain has been suggested, and if this can be controlled an enormous new supply of energy may be made available for industrial purposes. This would

\* Polissar, *J. Am. Chem. Soc.*, **58**, 1372 (1936).

† Ruben, Kamen, and Hassid, *J. Am. Chem. Soc.*, **62**, 3443 (1940).

‡ Turner *Rev. Modern Physics*, **12** (1940).



require the isolation of large quantities of the  $U^{235}$  isotope, since in ordinary uranium the much more abundant  $U^{238}$  nuclei break the chain by absorbing the neutrons before they can react with the  $U^{235}$  nuclei. A hydrogen-containing compound would have to be present to slow the neutrons. If this is water, the resultant steam can drive a turbine.

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### PROBLEMS

- Measurements on a certain radioelement gave a constant of  $1.65 \times 10^{-6}$  sec.<sup>-1</sup>.
  - What is its period of half-life?
  - What is its average life?
  - How long will it take for 99 per cent of the element to disintegrate?
  - What is the name of this radioelement?

Ans. (a) 4.85 days. (b) 7.0 days.  
(c) 32.2 days. (d) Radium E.
- Calculate: (a) the weight in grams of the radon in equilibrium with 1 g. of radium; (b) the volume occupied by this amount of radon under standard conditions of temperature and pressure.
 

Ans. (a)  $6.46 \times 10^{-8}$  g. (b) 0.652 cu. mm.
- Calculate the weight of radium E in equilibrium with 1 g. of radium D.
 

Ans.  $5.9 \times 10^{-4}$  g.
- Thorium B is an isotope of lead, and thus has nearly identical chemical and physical properties. A given quantity of thorium B was mixed with a lead salt containing 10 mg. of lead, taken into solution and precipitated as the chromate. Ten cubic centimeters of the supernatant liquid, when evaporated, gave a residue which was  $\frac{34}{100}$  as active as the original quantity of thorium B. What is the solubility of lead chromate in moles per liter?
 

Ans.  $2 \times 10^{-7}$  mole per liter.
- (a) Show mathematically that the radioactivity per micromole of a short-lived radio element is greater than that of a long-lived element.  
 (b) How many grams of radium will be required to give as much radioactivity for luminous paint as 1 g. of polonium?

6. A hospital maintained a solution containing 0.250 g. of radium as a source of radon for therapeutic purposes. The radon was pumped off under reduced pressure once a week.

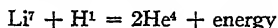
(a) How many grams of radon were obtained each week?

(b) What volume would it occupy under standard conditions of temperature and pressure?

7. The weight of lead in a sample of uraninite from the Black Hills of South Dakota was found to be 22.8 per cent of the weight of the uranium. Calculate from this fact a minimum age for the earth.

8. Alpha particles from radon have a velocity of  $1.6 \times 10^9$  cm. per sec. What voltage would have to be applied to protons to give the same energy?

9. Calculate the change in mass involved in the nuclear transformation (page 632)

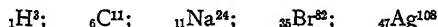


(a) How much energy is liberated in calories per mole?

(b) How much energy is liberated in electron volts?

(c) In what form is this energy liberated?

10. State what isotopic element may be produced when the following undergo radio disintegration.



11. (a) Calculate the packing fraction for helium. (b) Assuming that the mass lost during the combination of four hydrogen atoms to give a helium atom is converted into radiant energy according to the relation  $mc^2 = \epsilon = h\nu$ , calculate the wavelength of the resulting radiation.

12. A sample of radioactive sodium, with a half-life of 53,300 seconds, is injected into an animal. How many days will it take for the radioactivity to fall to one-tenth of its original intensity?

13. One kilogram of purified uranium is sealed in a vault as an indicator of time. If a chemist of the future finds 1 mg. of lead, what year A.D. will it be?

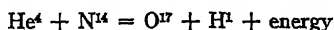
14. Actinium emanation comes in the group of rare gases, having zero valence. It loses an  $\alpha$  particle, the product loses another  $\alpha$  particle and then the new radioelement loses a  $\beta$  particle. (a) To what group in the periodic table does this radioelement belong? (b) Describe briefly its physical and chemical properties.

15. (a) After how many years will 1 g. of polonium decay to such a point that it is equivalent in radioactivity to 1 g. of radium?

(b) After ten years what will be the relative intensities of radio-activity of equal weights of radium and polonium?

16. If the products of a transmutation weigh 0.001 g. more per gram atom than the reactants, what is the minimum energy which must be supplied to effect the transmutation: (a) expressed in kilogram-calories per gram atom; (b) expressed in voltage which must be applied to a proton per transmutation?

17. Calculate the change in mass (page 632) and the energy involved in the nuclear transformation



18. How large would a proton current have to be in amperes in a high voltage transmutation apparatus in order to correspond to the number of alpha particles emitted by the radon in equilibrium with 1 gram of radium?

19. Radioactive phosphorus  $P^{30}$  can be prepared with the five different agencies,  $\alpha$ ,  $n$ ,  $p$ ,  $d$ , and  $\gamma$  rays. State what elements you would use for each process. Write the nuclear reaction in each case.

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20. Some unstable isotopes disintegrate with the emission of positrons and some with the emission of negative electrons. Considering the facts tabulated in this chapter, suggest a relation by means of which you can predict whether positrons or negative electrons will be emitted by an isotope of given mass.

21. (a) Beta particles have an initial velocity of about 0.3 the velocity of light. What voltage would have to be applied to electrons in order to be equivalent to beta rays?

(b) To how many beta particles per second would an electron current of 2 milliamperes correspond?

(c) To how many grams of radium B would this be equivalent?

22. Radio disintegration involves energies of the order of  $10^6$  electron volts. The extra energy involved in a 10-degree rise in temperature is negligible and the rate of nuclear reactions is independent of temperature. Nevertheless estimate the very small increase in the rate of a nuclear reaction involving  $10^6$  electron volts when the temperature is raised from  $25^\circ$  to  $35^\circ$ .

23. Write the equations for several different ways of producing radioactive aluminum using neutrons, deuterons, or  $\alpha$  particles.

## CHAPTER XXII

### ATOMIC STRUCTURE

The structure of the nucleus of the atom has been revealed through the study of radioactivity and through transmutation of elements by means of particles of high energy as described in the last chapter. The nuclear structures remain unchanged during all ordinary reactions and it is only the structure outside the nucleus which is of interest in ordinary chemistry. The position of an element in the periodic table and its chemical properties are determined by the extranuclear structure and this in turn depends on the magnitude of the positive charge on the nucleus (the atomic number). Before undertaking the study of this extranuclear structure, however, it is necessary to learn more of the nature of the electron.

**Conductance of Electricity through Gases.** Under ordinary conditions, gases are practically nonconductors of electricity, but when a sufficiently great difference of potential is established between two points within a gas, an electrical discharge takes place between the points. The potential necessary to produce such a discharge is quite high, forty thousand volts being required to produce a spark of one centimeter length in air at ordinary pressures. As the pressure of the gas is reduced progressively the spark becomes more uniform and broadens out. When a pressure of about 0.5 mm. is reached, the negative electrode, or *cathode*, appears to be surrounded by a thin luminous layer and between this and the anode is a series of luminous striations separated by dark regions, the number of which depends on the pressure, the kind of gas, and the dimensions of the vessel.

The current is carried between the electrodes partly by electrons and partly by gas ions. Positive gas ions are produced when molecules have their outer electrons removed, and negative ions are produced when the electrons become attached to other molecules. Gas ions, then, are similar to electrolytic ions, which have been studied in earlier chapters, but they are not governed by the usual valence rules. Mercury vapor, for example, can exist with 0, 1, 2, 3, etc., charges. Furthermore, the electrolytic ions are present before the passage of the electrical current but the gas ions are largely produced by the current itself, the few original electrons and ions acquiring sufficient

velocity in the electrical field to collide with neutral molecules and dislodge electrons from them. The dark spaces in the discharge tube indicate the regions where the electrons have not yet developed sufficient kinetic energy to ionize molecules. Light is produced when ions are discharged and electrons return toward their normal positions of lower energy level.

When the pressure is reduced below 0.01 mm. a new phenomenon is observed. The luminous columns disappear and the walls of the tube opposite the cathode become luminescent, the color of the luminescence depending on the nature of the glass. With soda glass the glow is greenish yellow, whereas with lead glass it is bluish. The luminescence is caused by the bombardment of the glass by negative particles or electrons projected from the cathode.

**Properties of Cathode Rays.** The discovery and interpretation of cathode rays by Sir. J. J. Thomson, Sir William Crookes, and others laid a foundation for much of the experimental work which led to rapid developments in our theories of atomic structure. It was found that an opaque object placed in the path of the cathode rays casts a shadow and that the rays travel in straight lines from the cathode. A small paddle wheel was made to revolve by the cathode rays, thus showing that the rays possess mechanical energy. If a concave cathode is used, the rays can be focused on a piece of platinum or other material so as to produce incandescence, thus showing that the rays possess considerable energy which can be converted into heat.

Although the cathode rays are stopped by most objects, they can penetrate very thin sheets of metal and other material. Lenard in 1894 demonstrated the passage of cathode rays through a thin aluminum window in the tube opposite the cathode. Coolidge\* developed a cathode-ray tube which can be used on a large scale for the production of cathode rays, the electrons passing through a considerable distance of air at ordinary pressures. The extent of the penetration depends on the density of the absorbing material and on the applied voltage.

The electrical properties of cathode rays are readily demonstrated by the fact that they are deflected in an electrostatic field toward the positive electrode, thus indicating a negative charge. When a magnetic field is applied at right angles to the rays, they are deflected in the direction which indicates that they are negative charges moving away from the cathode. When the magnetic field is reversed, the direction of deflection is reversed.

\* Coolidge, *J. Franklin Inst.*, **202**, 693-735 (1926).

**Properties of Electrons.** The velocity of electrons and the ratio of the mass to charge are determined in the apparatus shown in Fig. 159. Electrons are emitted from the cathode *C* and drawn to the anode *A* which is pierced by central holes 1 mm. in diameter. Another cylinder *B* is placed about 5 cm. away from *A*, the two holes being in exactly the same straight line, so that a very narrow bundle of rays may pass along the axis of the tube and fall upon the fluorescent screen at the opposite end of the tube. Upon this screen is a millimeter scale *S*. When a high potential is applied to the tube a phosphorescent spot appears at *F*. If a strong magnetic field is applied, the lines of force

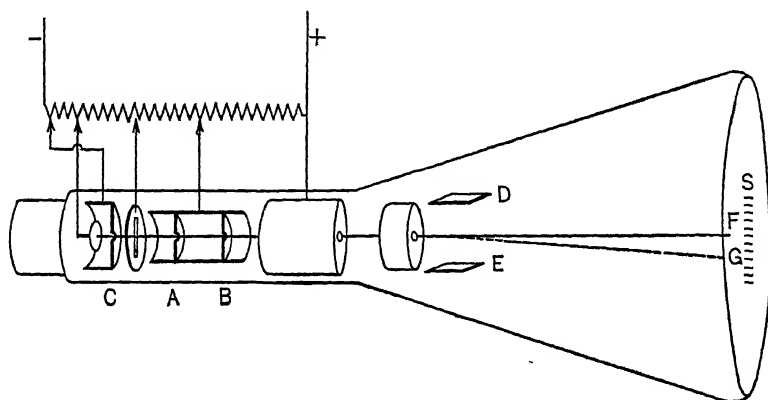


FIG. 159

being at right angles to the plane of the diagram, the rays will be deflected vertically, and the spot on the screen will move from *F* to *G*. Let *H* denote the strength of the magnetic field, and let *m*, *e*, and *v* represent, respectively, the mass, charge, and velocity of a cathode particle. A magnetic field, *H*, acting at right angles to the line of flight of the cathode particle will exert a force, *Hev*, which will tend to deflect the particle from a rectilinear path. This force must be equal to the centrifugal force of the moving particle acting outward along its radius of curvature. Therefore,

$$Hev = \frac{mv^2}{r} \quad [1]$$

or

$$Hr = \frac{mv}{e} \quad [2]$$

Since both *H* and *r* can be measured, the ratio *mv/e* can be determined.

Now if a difference of potential is established between the electrode plates,  $D$  and  $E$ , and the lines of force in the electrostatic field have the proper direction, it is possible to alter the strength of the field so as just to counterbalance the effect of the magnetic field, and bring the phosphorescent spot back to  $F$  again. Under these conditions, if  $X$  denotes the strength of the electrostatic field,

$$Xe = H\epsilon v \quad [3]$$

or

$$v = \frac{X}{H} \quad [4]$$

Since both  $X$  and  $H$  can be measured,  $v$  can be calculated, and, by introducing the value so obtained into equation (2), the ratio  $m/e$  can be evaluated. By this method, the value of  $v$  was found to be  $6 \times 10^9$  cm. per second, when the potential difference between  $C$  and  $A$  was 10,000 volts. The mean value of the most trustworthy

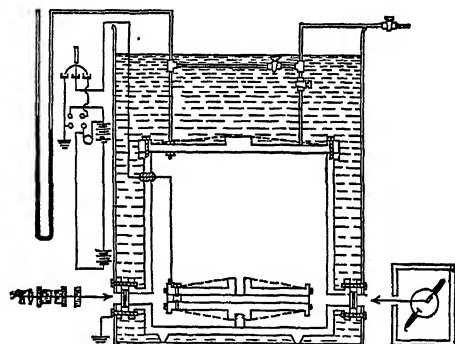


FIG. 160

determinations of the ratio  $m/e$  at low velocities was found to be  $5.685 \times 10^{-8}$  gram per electromagnetic unit. At velocities approaching the velocity of light the mass increases and approaches infinity as predicted by the theory of relativity.

The charge on an electron has been determined by Millikan\* using the apparatus shown in Fig. 160. A spray of finely divided oil, or some other liquid, is introduced into a thermostated chamber by means of an atomizer until one of the tiny drops eventually finds its way through the aperture, into the space between the two horizontal condenser plates. The hole is then closed, and the air between the plates is ionized by means of the x-ray tube. A lamp at the left

\* Millikan, *Phys. Rev.*, **39**, 349 (1911); **2**, 109 (1913).

illuminates the drop, and its motion is observed through a microscope, not shown in the figure. The eyepiece of the microscope is fitted with an engraved glass scale, which enables the observer to measure accurately the motion of the drop. When the drop collides with one of the ions of the air in the condenser chamber, it absorbs the ion and acquires an electric charge, the sign of which will determine the subsequent direction of its motion with reference to the plates. By means of the switch the signs of the charges on the two plates can be reversed, thus causing a corresponding reversal of the direction of motion of the drop. Any change in the speed of the drop is an indication of a change in the charge which it carries. Therefore, since the speed with which the drop moves is directly proportional to the magnitude of its charge, it follows that, by measuring the change of speed and comparing it with the speed of the drop when falling under the influence of gravitational attraction alone, the value of the charge carried by the drop can be calculated.

Millikan observed that several different charges were quite commonly acquired by a single drop, but in every case the total charge was invariably an exact integral multiple of an elemental charge,  $e$ . The value of  $e$  obtained in this way and corrected for recent measurements on the viscosity of air is  $4.80 \times 10^{-10}$  absolute electrostatic unit.

**Avogadro's Constant.** The measurement of the charge on the electron gives an accurate method for calculating *Avogadro's constant*. In making these calculations it is necessary to use uniform units, and it should be emphasized that the practical unit of electrical charge, the coulomb, is one-tenth of the electromagnetic unit and that a charge expressed in electromagnetic units (emu.) is converted into electrostatic units (esu.) by multiplying by the velocity of light ( $2.998 \times 10^{10}$ ). Then,

$$\begin{aligned} \text{Charge on electron} &= 4.80 \times 10^{-10} \text{ esu.} = 1.601 \times 10^{-20} \text{ emu.} \\ &= 1.601 \times 10^{-19} \text{ coulomb} \end{aligned} \quad [5]$$

It is found by experiment that 1 gram-equivalent of hydrogen is liberated during electrolysis by 96,500 coulombs of electricity. Therefore, for hydrogen ions

$$\frac{m}{e} = \frac{1.0080 \text{ g.}}{9650 \text{ emu.}} = 1.045 \times 10^{-4} \quad [6]$$

Since the charge of the hydrogen ion is the same as that of the electron, namely,  $1.601 \times 10^{-20}$  emu., but opposite in sign,

$$m = 1.045 \times 10^{-4} \times 1.601 \times 10^{-20} = 1.673 \times 10^{-24} \text{ g.} \quad [7]$$



The Avogadro number, the number of atoms in a gram-atom, then is

$$\frac{1.008}{1.673 \times 10^{-24}} = 6.03 \times 10^{23} \quad [8]$$

After the weight of a single atom of hydrogen has been established, the weight in grams of any other atom may be determined from its atomic weight.

The mass of the electron can be determined also. Since  $e$  is the same for the hydrogen ion and the electron, and since  $m/e$  is  $5.685 \times 10^{-8}$  g. per emu. for the electron and  $1.045 \times 10^{-4}$  for the hydrogen ion, it follows that the mass of the electron is  $1/1833$  the mass of the hydrogen ion. Since the latter is 1.0080 on the scale of atomic weights, the electron must have an "atomic" weight of 0.000548.

**X Rays and Atomic Numbers.** The wavelength of x rays is determined by using a crystal as a diffraction grating as described on page 44. The wavelength depends on the applied voltage but when the voltage is kept constant the characteristic x radiation is determined by the elements of which the target is composed, and its penetrating power increases with the atomic weight of the radiating element. Most of the properties of the elements such as volume, heats of reaction, and standard electrode potentials are periodic functions of the atomic weights, but the wavelengths of x rays generated by targets of the different elements are not a periodic function but a continuous function of the number of the element when the elements are arranged in order of increasing atomic weights.\*

Moseley placed different metals as targets in an x-ray tube and determined the wavelength of the characteristic x rays using the plane of a crystal for a reflection grating. With increasing atomic number, the series of lines constituting the simple x-ray spectrum of the elements was found to undergo a gradual shift in the direction of shorter wavelengths. Furthermore, the elements of higher atomic numbers were found to give two new series of characteristic lines of longer wavelength, and these also underwent a displacement in the direction of shorter wavelengths as the atomic number of the element increased. These three series of lines have been designated the " $K$ ," " $L$ ," and " $M$ " series, respectively, and they in turn consist of several lines the prominent doublets of which are designated by  $\alpha$  and  $\beta$ .

Moseley discovered that a very simple numerical relationship exists between the frequency of corresponding lines in the x-ray spectra of different elements and their atomic numbers. This relationship may

\* Moseley, *Phil. Mag.*, **26**, 210 (1913); **27**, 703 (1914).

be expressed by the equation

$$\sqrt{\nu} = A(Z - b), \quad [9]$$

where  $\nu$  is the frequency and  $Z$  the atomic number of the element, and where  $A$  and  $b$  are constants. This law has been found to hold equally well for the  $K$ ,  $L$ , and  $M$  series, as shown graphically in Fig. 161. It has been shown, however, that the square root of the frequency is not exactly a linear function of the atomic number  $Z$ .

The atomic number is obtained by starting with the lightest element, hydrogen, as 1 and counting the elements 1, 2, 3, 4, etc., as they occur

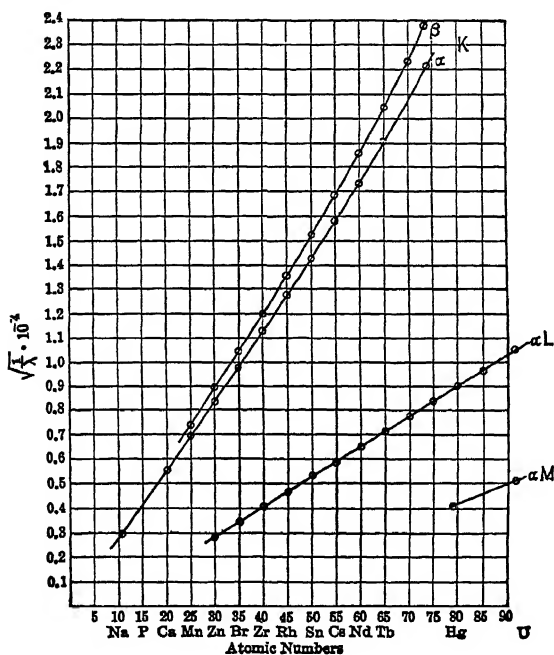


FIG. 161

in the periodic table in order of increasing atomic weights. When the atomic weight does not give the exact order which is expected from the chemical properties, as in the case of tellurium and iodine, the order is taken to agree with the position in the periodic table.

This *atomic number* is a fundamental constant. It is equal to the positive charge on the nucleus of the atom which in turn is the same as the number of electrons surrounding the nucleus in the uncharged atom.

The arrangement of elements according to their atomic numbers

straightened out certain anomalies in the periodic table. Potassium follows argon, nickel follows cobalt, and iodine follows tellurium, in spite of the fact that classification by atomic weights puts them in the reverse order. The existence of nuclei with different weights but the same atomic number explains why this order is reversed and shows that the atomic number is a more fundamental property than the atomic weight. When Moseley prepared his table of atomic numbers in 1914, there were six gaps corresponding to six missing elements but five of these have since been filled. Before the discovery of Moseley's relation there was doubt concerning the number of rare earth elements because the chemistry of these elements is so much alike. Referring to a graph like that of Fig. 161 it was found that, to make the line continuous, there should be fourteen rare earth elements; also a homologue of zirconium between barium and tantalum. Thirteen of these positions could be filled from rare earth metals then known and the homologue of zirconium was found by Coster and Hevesy, and called hafnium.

The elements of even atomic number in the earth's crust and in meteorites are much more abundant than those of odd atomic number. A more stable nucleus is suggested not only by this fact but also by the fact that the radioactive elements of even atomic number have longer lives.

**The Mass Spectrometer.** Cathode rays consist of negatively charged particles which are repelled from the cathode of a vacuum tube. These particles, or electrons, under the influence of a high potential, move with a high velocity, and, by collision with the atoms of the residual gas in the tube, they remove one or more electrons from molecules, leaving them with a positive charge. These positively charged atoms are immediately repelled by the anode, and move with high velocity toward the cathode. If a tube with a perforated cathode is used, the positively charged units, or gaseous ions, will pass through the perforations into the space behind the cathode, where their properties may be studied. These rays were called *positive rays* by Sir J. J. Thomson, who developed an ingenious method for the determination of the individual masses of the positively charged particles by sifting them out into parabolic curves with the help of a magnetic field combined with an electrostatic field.

Aston in 1919 developed a mass spectrograph for separating the atoms of different mass so that they can be recorded with a photographic plate or an ionization chamber. The mass spectrograph has been constantly improved until now it can give the atomic masses

with great accuracy — considerably greater than that obtained by chemical means. In Aston's\* apparatus the positive rays pass through parallel slits and are spread out by passage through an electrostatic field between two charged plates. The particles are then deflected in the opposite direction by a strong magnetic field and the two fields are so adjusted that the positively charged particles are focused on a photographic plate. The particles with large values of  $e/m$  are deflected most in both fields and there is a sifting out of the particles according to the ratio of charge to mass. The spectrogram thus produced is calibrated with photographic lines obtained with particles of known masses. Care is necessary in the interpretation of results because the particles may have two or more charges and there may be ionized fragments of molecules such as  $\text{CH}^+$ ,  $\text{CH}_2^+$  and  $\text{CH}_3^+$ ; or hydrides may be formed with impurities of hydrogen.

A somewhat different type of spectrograph, shown in Fig. 162, has been developed by Bainbridge.† A beam of positive ions is produced in an electrical discharge tube and thrown out through the slits  $s_1$  and  $s_2$ . The particles then pass through the electrostatic field  $X$  between  $E_1$  and  $E_2$ , at right angles to which there is also an electromagnetic field  $H$ . Only those ions which have a velocity which is equal to  $X/H$  will pass through slit  $s_3$ ; the others will all curve around so as to miss the exit slit. All ions that do get through have the same velocity and they are curved around by a powerful magnetic field through an arc of  $180^\circ$  so as to hit the photographic plate  $P$ .

The radius of curvature of the ion beam represented by  $R$  is given by the relation

$$R = \frac{mv}{eH} \quad [10]$$

Since the charge on the ion, the magnetic field, and the velocity are

\* Aston, "Mass Spectra and Isotopes," E. Arnold and Co., London, 1933.

† Bainbridge, *J. Franklin Inst.*, 215, 509 (1933).

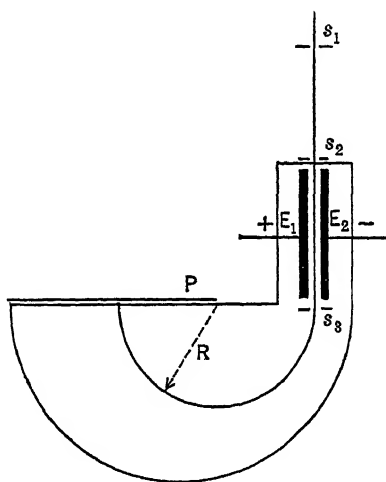


FIG. 162

all constant, the radius or the position on the photographic plate is directly proportional to the mass. The plate is calibrated with ions of known mass.

For quantitative work, it is important to know not only what isotopes are present but also the relative abundance. The blackening on a photographic plate is only a rough measure of the number of ions hitting the plate at a given position, and so it is necessary to use an electrical method in which all the ions entering a slit are caught in a "Faraday cage" and the charges leak off through an electric circuit. The feeble currents are amplified with electron tubes and read with a galvanometer. Instead of moving the slit along to intercept ion beams having different ratios of  $m/e$ , it is simpler to change the accelerating voltage. The galvanometer reading at a setting of a given isotope is a measure of the number of ions and the ratio of peaks in the ionization current is a direct measure of the ratio of the abundance of the isotopes.

In Fig. 163 the first two mass spectrograms are taken from measurements of Aston on the isotopes of chlorine and the fragments of methane produced by the action of electrons on methane. The mass spectrometer has not yet received the attention which it deserves in studying the products of the decomposition of gaseous materials.

The isotopes of chlorine 35 and 37 and the corresponding hydrides 36 and 38 are clearly shown. In the second spectrogram the slight difference in mass between oxygen and methane is evident.

In the lowermost figure, taken from the work of Nier,\* the relative abundance of the different isotopes of lead is given by the heights of the peaks obtained when the galvanometer deflections are plotted against the mass of the isotopes.

The mass spectrometer developed by Nier† is convenient for determining isotope ratios in tracer experiments. Metal chambers and slit systems are attached with Kovar seals to a long tube of glass, with a curve in the middle which passes between the V-shaped poles of an electromagnet. Less than a milligram of material is needed for an analysis and when the spectrometer is operating properly analysis may be made rapidly with an error of less than 0.1 per cent in the abundance ratio.

**Occurrence of Isotopes.** The development of the mass spectrograph as a precision instrument has led to the discovery of a large number of isotopes. There are in all 92 elements of different atomic numbers, up to and including uranium.

\* Nier, *J. Am. Chem. Soc.*, **60**, 1572 (1938).

† Nier, *Rev. Sci. Inst.*, **11**, 212 (1940).

The reference standard for chemical atomic weights is ordinary oxygen taken as 16, which is really a mixture of isotopes with the distribution  $O^{16} = 540 : O^{17} = 0.02 : O^{18} = 1$ . The reference standard for the mass numbers, obtained with the mass spectrometer, is the lightest isotope of oxygen  $O^{16}$ . It is a more definite standard than the ordinary

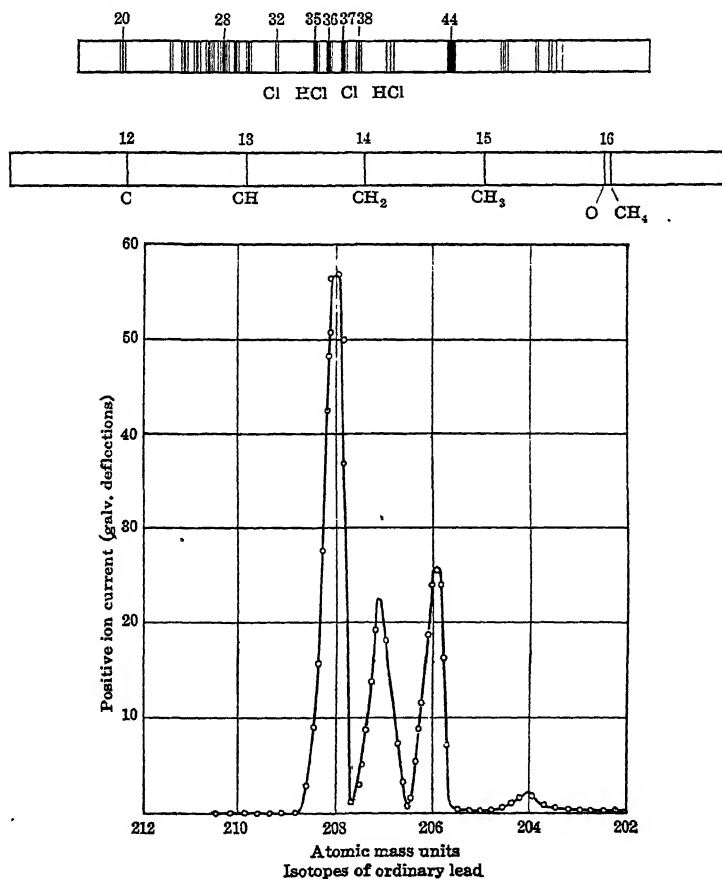


FIG. 163

oxygen in which the isotope ratios may change slightly. Moreover, the atomic masses can be determined with the mass spectrometer with greater accuracy than the chemical atomic weights can be determined by chemical analysis; but in all chemical and physical chemical calculations the chemical atomic weights are used.

Since the standard of atomic *mass*  $O^{16}$  is lighter than the mixture of oxygen isotopes, the atomic masses are lighter than the correspond-

ing chemical atomic *weights*. They are lighter in the ratio 1/1.00027.

It has been known since 1913 that the atomic weight of lead can vary, depending on the source of the material. Lead obtained for example from a radioactive ore rich in uranium has a lower atomic weight than lead which is derived in part from the radio-disintegration of thorium. This situation will be understood by reference to Fig. 157. Moreover, it has been pointed out by Urey that in the lighter elements the atomic weight measurements have about reached the limit of useful accuracy and that if further accuracy is obtained it will be necessary to take account of the concentration of isotopes which inevitably accompanies the chemical and physical operations of purification and analysis.

In Table I are listed a few of the lighter elements with their exact atomic masses obtained on the basis of mass spectrometer data and a statement of the relative abundance of the different isotopes.

TABLE I  
STABLE NUCLEI OF SOME OF THE LIGHTER ELEMENTS

Nucleus	Atomic Mass	Relative Abundance	Nucleus	Atomic Mass	Relative Abundance
${}^1_1\text{H}^1$	1.0081	99.98	$\text{C}^{12}$	12.0040	98.9
${}^1_1\text{H}^2$	2.0147	0.02	$\text{C}^{13}$	13.0076	1.1
${}^2_2\text{He}^4$	4.0039	100.00	$\text{N}^{14}$	14.0075	99.62
${}^3_3\text{Li}^7$	7.0182	92.1	$\text{N}^{15}$	15.0049	0.38
$\text{O}^{16}$	16.0000	99.76	$\text{Cl}^{35}$	34.9813	75.4
$\text{O}^{17}$	17.0040	0.04	$\text{Cl}^{37}$	36.9788	24.6
$\text{O}^{18}$	18.00369	0.2			

In Table II most of the elements are listed in order of their atomic number, together with their chemical atomic weights (1941). The stable isotopes for each element are recorded in order of relative abundance.

Isotopes may be detected and their relative amounts estimated not only with the mass spectrograph but also with the ordinary optical spectrograph. The band spectra depend in part on the moment of inertia of the atom pair which is responsible for the band, and this in turn depends on the mass of the atoms. One of the first applications of this principle to the detection of isotopes was in the infrared absorption spectrum of hydrochloric acid. The superimposed spectra indicating the two different isotopes of chlorine are clearly shown in the lower left spectrogram in Fig. 146. More recently the spectrum of  $\text{H}^2\text{Cl}^{35}$  has been determined and it is shifted, in agreement with theoretical predictions, by more than  $1\ \mu$  toward the longer wavelengths.

TABLE II  
STABLE ISOTOPES AND ATOMIC WEIGHTS

Element	Atomic Number	Atomic Weight	Mass Numbers of Isotopes in Order of Abundance
Hydrogen	1	1.0080	1, 2
Helium	2	4.003	4, 3
Lithium	3	6.940	7, 6
Beryllium	4	9.02	9
Boron	5	10.82	11, 10
Carbon	6	12.010	12, 13
Nitrogen	7	14.008	14, 15
Oxygen	8	16.0000	16, 18, 17
Fluorine	9	19.00	19
Neon	10	20.188	20, 22, 21
Sodium	11	22.997	23
Magnesium	12	24.32	24, 25, 26
Aluminum	13	26.97	27
Silicon	14	28.06	28, 29, 30
Phosphorus	15	30.98	31
Sulfur	16	32.06	32, 34, 33, 36
Chlorine	17	35.457	35, 37
Argon	18	39.944	40, 36, 38
Potassium	19	39.096	39, 41, 40*
Calcium	20	40.08	40, 44, 42, 48, 43, 46
Scandium	21	45.10	45
Titanium	22	47.90	48, 46, 47, 49, 50
Vanadium	23	50.95	51
Chromium	24	52.01	52, 53, 50, 54
Manganese	25	54.93	55
Iron	26	55.85	56, 54, 57, 58
Cobalt	27	58.94	59
Nickel	28	58.69	58, 60, 62, 61, 64
Copper	29	63.57	63, 65
Zinc	30	65.38	64, 66, 68, 67, 70
Gallium	31	69.72	69, 71
Germanium	32	72.60	74, 72, 70, 73, 76
Arsenic	33	74.91	75
Selenium	34	78.96	80, 78, 76, 82, 77, 74
Bromine	35	79.916	79, 81
Krypton	36	83.7	84, 86, 82, 83, 80, 78
Rubidium	37	85.48	85, 87*
Strontium	38	87.63	88, 86, 87, 84
Yttrium	39	88.92	89
Zirconium	40	91.22	90, 92, 94, 91, 96
Columbium	41	92.91	93
Molybdenum	42	95.95	98, 96, 95, 92, 97, 94, 100
Ruthenium	44	101.70	102, 101, 104, 100, 99, 96
Rhodium	45	102.91	103
Palladium	46	106.70	108, 108, 105, 110, 104, 102
Silver	47	107.880	107, 109
Cadmium	48	112.41	114, 112, 111, 110, 113, 116, 106, 108
Indium	49	114.76	115, 113
Tin	50	118.70	120, 118, 116, 119, 117, 124, 122, 112, 114, 115
Antimony	51	121.76	121, 123
Tellurium	52	127.61	130, 128, 126, 125, 124, 122, 123, 120
Iodine	53	126.92	127
Xenon	54	131.3	132, 129, 131, 134, 136, 130, 128, 124, 126
Cesium	55	132.91	133
Barium	56	137.36	138, 137, 136, 135, 134, 130, 132
Lanthanum	57	138.92	139
Cerium	58	140.13	140, 142, 138, 136
Praseodymium	59	140.92	141
Neodymium	60	144.27	142, 144, 146, 143, 145, 148, 150
Tungsten	74	183.92	184, 186, 182, 183, 180
Rhenium	75	186.31	187, 185
Osmium	76	190.2	192, 190, 189, 188, 187, 186, 184
Iridium	77	193.1	193, 191
Platinum	78	195.23	195, 194, 196, 198, 192
Gold	79	197.20	197
Mercury	80	200.61	202, 200, 199, 201, 198, 204, 196
Thallium	81	204.39	205, 203
Lead	82	207.21	208, 206, 207, 204
Bismuth	83	209.00	209
Thorium	90	232.12	232*
Uranium	92	238.07	238, * 235, * 234*

\*Naturally radioactive.



The presence of oxygen isotopes having masses of 16, 17, and 18 was discovered by a study of bands in the absorption spectrum of the sun as its light passed through the atmosphere surrounding the earth. The heavier isotope of hydrogen, deuterium, was discovered by the appearance of a new, neighboring line in the emission spectrum after continued fractional distillation of hydrogen. The discovery of the heavier isotope of carbon,  $C^{13}$ , is shown in Fig. 164. This spectrogram,

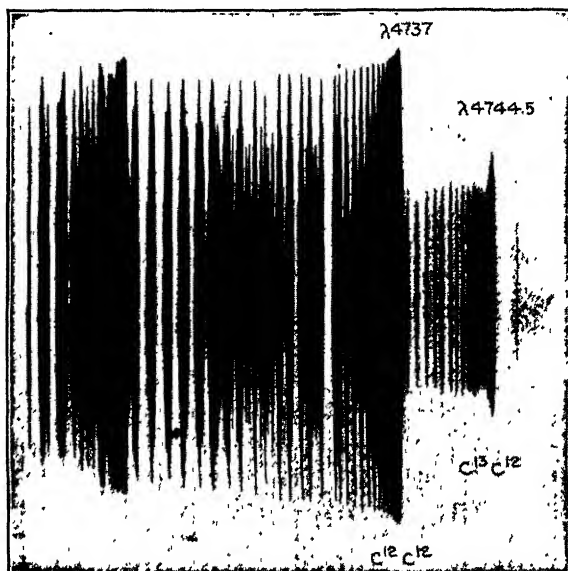


FIG. 164

reproduced with the permission of the University of Chicago Press, was obtained by King and Birge\* in carbon vapor at high temperatures. The band of lesser intensity due to the molecule  $C^{12}-C^{13}$  is plainly evident at the right.

**Concentration of Isotopes.** The ratio of isotopes may be altered by fractional diffusion or evaporation, or by centrifuging, or, in fact, by any physical or chemical method which makes use of the difference in weights. It will be remembered that the relative velocities of molecules are inversely proportional to the square roots of the molecular weights. Effective concentration of small quantities of isotopes has been accomplished in the lighter elements with a battery of mercury diffusion pumps operating in series.† The separation of

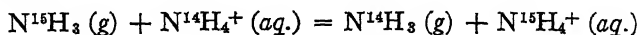
\* King and Birge, *Astrophysical Journal*, **72**, 24 (1930).

† Hertz, *Z. Physik*, **79**, 108 (1932).

isotopes by means of the mass spectrograph would seem to be a simple matter but the difficulty lies in obtaining an ionization current large enough to give a usable supply of different isotopes. The effect on the photographic plate is of course greatly magnified by the development of the plate.

One of the simplest methods for concentrating isotopes combines thermal diffusion and convection. When a vertical central wire or tube is maintained at a temperature 200 or 300° above the walls of a larger containing tube and allowed to stand, the heavier constituents of an enclosed gas concentrate at the bottom of the tube.\* Bromine and air in a glass tube can be seen to separate within a few minutes. In such a tube 60 ft. high filled with methane the carbon at the bottom of the tube becomes enriched with C<sup>13</sup> in a few weeks from 1 per cent to several per cent, and by flowing through slowly at the top a fresh supply of methane it is possible to draw off at the bottom over 100 ml. per day of the methane enriched with C<sup>13</sup>†.

Isotopes may be separated also by chemical means, although isotopes were originally thought to have identical chemical properties. The natural vibration frequency of atoms in a molecule depends to a slight extent on the mass of the atoms involved and this vibration frequency affects the "zero point energy," or the energy requirement at the very bottom of the Morse curve shown in Fig. 149. In other words, there is a very slight difference in the activation energies for chemical reactions involving the isotopes. In competing reactions, then, the heavier isotope should react somewhat more slowly. The difference is sufficient for complete separation in the case of hydrogen where the masses are 1 and 2, but there is a chance also for a slight concentration of isotopes in the other light elements. This slight difference in reactivity shows up also in the position of chemical equilibrium.‡ For example, the equilibrium constant for the reaction



is not unity; calculations show that it is 1.033. Thode and Urey§ carried out experimental concentration of N<sup>15</sup> using this reaction in an effective column passing the ammonia gas up against a stream of ammonium nitrate flowing down. Concentration of N<sup>15</sup> up to 72 per cent was obtained and the experimentally determined value of K was

\* Clusius and Dickel, *Naturwiss.*, **26**, 546 (1938); **27**, 149 (1938); Brewer and Bramley, *Phys. Rev.*, **55**, 590 (1939).

† Taylor and Glochler, *J. Chem. Phys.*, **7**, 350 (1939); **8**, 843 (1940).

‡ Urey and Greiff, *J. Am. Chem. Soc.*, **57**, 321 (1935).

§ Thode and Urey, *J. Chem. Phys.*, **7**, 34 (1939).

1.023. It is now possible to purchase\* small quantities of ammonium nitrate containing 30 per cent of the nitrogen as  $N^{15}$ . Urey has obtained  $C^{13}$  in high concentrations also, using large absorption towers with HCN gas and NaCN solution.

Heavy nitrogen, heavy carbon, and heavy oxygen have been used effectively as tracer elements in physical chemical and biochemical investigations. The positions in a molecule or an organism taken by these tagged atoms can be ascertained with the help of a mass spectrometer which gives the ratio of the heavy isotope to the common isotope. For example, previously unavailable information has been found with the help of  $N^{15}$ , concerning the biochemical behavior of certain amino acids and proteins.†

It is likely that all the slight differences in chemical behavior of isotopes, which makes their separation possible, have not yet been explored. The kinetic method, utilizing competing reactions which are not in equilibrium, should be investigated.

**Deuterium.**‡ A simple and effective means of separating the isotopes of hydrogen in these competitive reactions was found in the electrolysis of water.§ Ordinary hydrogen contains 1 part of  $H^2$  in about 6000 parts of  $H^1$ , and by electrolyzing away most of the water in a given sample the residue of water, i.e., the last hydrogen to come off in the electrolysis, is much richer in  $H^2$ .|| Continuing the process on a large scale it has been possible to provide practically pure  $H_2^2$  or  $H_2^{20}$  as an ordinary, not too expensive chemical.

The properties of this heavy isotope of hydrogen are so different from ordinary hydrogen that a special name was assigned to it—deuterium. The symbol for deuterium is D. The properties of water and heavy water are compared in Table III.

Many uses have been developed for deuterium but thus far they have been restricted to the laboratory. Its use as a projectile in nuclear disintegrations has been stressed already. By substituting deuterium for hydrogen, large band shifts are produced and it is thus possible to connect spectral bands with definite bonds in the molecule. A large variety of new organic compounds has been synthesized in which deuterium takes the place of hydrogen. Perhaps the greatest opportunity with the new material lies in the ability to mark hydrogen

\* Eastman Kodak Co.

† Schoenheimer and Rittenberg, *J. Biol. Chem.*, **127**, 285 (1939).

‡ Urey and Teal, "Heavy Hydrogen," *Rev. Modern Physics*, **7**, 34 (1935); Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, Cambridge, 1935.

§ Washburn and Urey, *Proc. Nat. Acad. Sci.*, **18**, 496 (1932).

|| Lewis, *J. Am. Chem. Soc.*, **55**, 1297 (1933).

atoms and follow them through chemical and biological reactions.

The movement of the heavier isotope to different chemical substances or to different parts of an organism can be followed simply by making accurate density measurements of the water produced by oxidation of the hydrogen and deuterium. Many hypotheses of chemical kinetics can now be subjected to experimental test. In one

TABLE III  
PROPERTIES OF D<sub>2</sub>O AND H<sub>2</sub>O

	Specific Gravity 20°	Freezing Point	Boiling Point	Heat Vaporization per Mole	Surface Tension 20°	Viscosity 20° × 10 <sup>3</sup>	Dielectric Constant	Refractive Index $n_D^{20}$	Solubility NaCl grams per 1000 g.
D <sub>2</sub> O	1 1059	3 82°	101 42°	9960	67 8	12 6	80 5	1.32844	305
H <sub>2</sub> O	0 9982	0 00	100 00	9700	72 75	10 09	82.0	1.33300	359

of the first experiments of this type ordinary sugar was dissolved in heavy water and the water distilled off. The density of this water was less than before showing that some of the deuterium of the water had exchanged with hydrogen of the sugar. Quantitative measurements showed that half of the hydrogen atoms of the sugar had exchanged with deuterium. It is known from the structure of sugar that half of the hydrogens are attached to carbon and half to oxygen. It is concluded that those hydrogens attached to oxygen ionize and mix with the deuterium ions of the water, but that the hydrogen atoms attached directly to carbon do not ionize and are unable to leave the sugar molecule.

**Extranuclear Structure.** There are four fundamental experiments on which theories of atomic structure are based. The disintegration of the radioactive elements and the artificial disintegration of the light elements indicate that the nuclei of heavy atoms are composed of smaller more fundamental units. The occasional, abnormal deflection of alpha particles shows that the mass of the atom must be concentrated in a nucleus occupying but a small fraction of the total atom. The mass spectrograph gives a measure of the mass of the nucleus; and the x-ray measurements of the atomic number reveal the number of excess positive charges on the nucleus, and the number of electrons surrounding the nucleus. The atomic number is of the greatest interest in chemistry, for the number and arrangement of these extranuclear electrons determines the position of an element in the periodic table and its chemical properties. The familiar periodic table of the elements was given in Table I on page 7 where the atomic numbers are shown in heavy type and the atomic weights in lighter type.

The first, second, third, and fourth electron shells are known as

the  $K, L, M, N$  shells. They correspond to the  $K, L, M, N$  series in the x-ray spectra discussed on page 626. They stand for different values of the first or principal quantum number  $n$ . For  $K, n = 1$ ; for  $L, n = 2$ ; for  $M, n = 3$ , etc.  $K$  radiation is involved when the target is bombarded with cathode rays of sufficient velocity to displace electrons from the innermost shell. The  $L$  series of x-ray spectral lines is emitted when electrons fall back from outer shells into positions in the second shell from which electrons have been displaced by x-ray bombardment, or left vacant when the  $L$  electron falls back to the  $K$  shell.

The rare gases are the key elements in the periodic table for they represent the completion of a shell. The number of elements in a shell is limited by the quantum numbers as described on page 559. The assignments of all the quantum numbers of the elements are given in Table IV where the first two quantum numbers are given at the top of the table and the electrons having different third and fourth quantum numbers are given in the vertical column.

The number of elements between the rare gases are  $2(\text{H-He})$ ;  $8(\text{He-Ne})$ ;  $8(\text{Ne-A})$ ;  $18(\text{A-Kr})$ ;  $18(\text{Kr-Xe})$ ;  $32(\text{Xe-Rn})$  as can be determined from the first column of Table IV or from Table III on page 560. Attention was first called to this sequence of numbers by Rydberg in 1914 who pointed out that they are  $2 \times 1^2$ ;  $2 \times 2^2$ ;  $2 \times 3^2$ ; and  $2 \times 4^2$ . By comparing these two tables it is seen that when the first quantum number is 1 the second must be 0, and the third must be 0 but the fourth can have two values ( $+\frac{1}{2}$  and  $-\frac{1}{2}$ ), without violating the Pauli principle. This leaves places in the periodic table for two different elements, and they are occupied by hydrogen and helium.

When  $n = 2, l$  can be either 1 or 0;  $m_l$  can have four different possible values each with two different values of  $m_s$ . Thus there is room for eight elements, as shown in Table IV, for the group which has 2 for a principal quantum number. The number of possible elements of other groups can be calculated in a similar manner.

TABLE IV

QUANTUM NUMBERS AND THE ARRANGEMENT OF ELECTRONS IN THE ELEMENTS

		K	L	M	N	O	P	Q
Atomic Number	Element	1 <i>s</i>	2 <i>s p</i>	3 <i>s p d</i>	4 <i>s p d f</i>	5 <i>s p d f</i>	6 <i>s p d f</i>	7 <i>s</i>
1	H	1						
2	He	2						
3	Li	2	1					
4	Be	2	2					
5	B	2	2 1					
6	C	2	2 2					
7	N	2	2 3					
8	O	2	2 4					
9	F	2	2 5					
10	Ne	2	2 6					
11	Na	2	2 6	1				
12	Mg	2	2 6	2				
13	Al	2	2 6	2 1				
14	Si	2	2 6	2 2				
15	P	2	2 6	2 3				
16	S	2	2 6	2 4				
17	Cl	2	2 6	2 5				
18	A	2	2 6	2 6				
19	K	2	2 6	2 6	1			
20	Ca	2	2 6	2 6	2			
21	Sc	2	2 6	2 6 1	2			
22	Ti	2	2 6	2 6 2	2			
23	V	2	2 6	2 6 3	2			
24	Cr	2	2 6	2 6 5	1			
25	Mn	2	2 6	2 6 5	2			
26	Fe	2	2 6	2 6 6	2			
27	Co	2	2 6	2 6 7	2			
28	Ni	2	2 6	2 6 8	2			
29	Cu	2	2 6	2 6 10	1			
30	Zn	2	2 6	2 6 10	2			
31	Ga	2	2 6	2 6 10	2 1			
32	Ge	2	2 6	2 6 10	2 2			
33	As	2	2 6	2 6 10	2 3			
34	Se	2	2 6	2 6 10	2 4			
35	Br	2	2 6	2 6 10	2 5			
36	Kr	2	2 6	2 6 10	2 6			
37	Rb	2	2 6	2 6 10	2 6	1		
38	Sr	2	2 6	2 6 10	2 6	2		
39	Y	2	2 6	2 6 10	2 6 1	2		
40	Zr	2	2 6	2 6 10	2 6 2	2		
41	Cb	2	2 6	2 6 10	2 6 4	1		
42	Mo	2	2 6	2 6 10	2 6 5	1		
43	(Ma)	2	2 6	2 6 10	2 6 5	2		
44	Ru	2	2 6	2 6 10	2 6 7	1		
45	Rh	2	2 6	2 6 10	2 6 8	1		
46	Pd	2	2 6	2 6 10	2 6 10			

TABLE IV — *Continued*

## QUANTUM NUMBERS AND THE ARRANGEMENT OF ELECTRONS IN THE ELEMENTS

		K	L	M	N	O	P	Q
Atomic Number	Element	1 <i>s</i>	2 <i>s p</i>	3 <i>s p d</i>	4 <i>s p d f</i>	5 <i>s p d f</i>	6 <i>s p d f</i>	7 <i>s</i>
47	Ag	2	2 6	2 6 10	2 6 10	1		
48	Cd	2	2 6	2 6 10	2 6 10	2		
49	In	2	2 6	2 6 10	2 6 10	2 1		
50	Sn	2	2 6	2 6 10	2 6 10	2 2		
51	Sb	2	2 6	2 6 10	2 6 10	2 3		
52	Te	2	2 6	2 6 10	2 6 10	2 4		
53	I	2	2 6	2 6 10	2 6 10	2 5		
54	Xe	2	2 6	2 6 10	2 6 10	2 6		
55	Cs	2	2 6	2 6 10	2 6 10	2 6	1	
56	Ba	2	2 6	2 6 10	2 6 10	2 6	2	
57	La	2	2 6	2 6 10	2 6 10	2 6 1	2	
58	Ce	2	2 6	2 6 10	2 6 10 1	2 6 1	2	
59	Pr	2	2 6	2 6 10	2 6 10 2	2 6 1	2	
60	Nd	2	2 6	2 6 10	2 6 10 4	2 6	2	
61	(II)	2	2 6	2 6 10	2 6 10 5	2 6	2	
62	Sm	2	2 6	2 6 10	2 6 10 6	2 6	2	
63	Eu	2	2 6	2 6 10	2 6 10 7	2 6	2	
64	Gd	2	2 6	2 6 10	2 6 10 7	2 6 1	2	
65	Tb	2	2 6	2 6 10	2 6 10 8	2 6 1	2	
66	Dy	2	2 6	2 6 10	2 6 10 10	2 6	2	
67	Ho	2	2 6	2 6 10	2 6 10 11	2 6	2	
68	Er	2	2 6	2 6 10	2 6 10 12	2 6	2	
69	Tm	2	2 6	2 6 10	2 6 10 13	2 6	2	
70	Yb	2	2 6	2 6 10	2 6 10 14	2 6	2	
71	Lu	2	2 6	2 6 10	2 6 10 14	2 6 1	2	
72	Hf	2	2 6	2 6 10	2 6 10 14	2 6 2	2	
73	Ta	2	2 6	2 6 10	2 6 10 14	2 6 3	2	
74	W	2	2 6	2 6 10	2 6 10 14	2 6 4	2	
75	Re	2	2 6	2 6 10	2 6 10 14	2 6 5	2	
76	Os	2	2 6	2 6 10	2 6 10 14	2 6 6	2	
77	Ir	2	2 6	2 6 10	2 6 10 14	2 6 9	1	
78	Pt	2	2 6	2 6 10	2 6 10 14	2 6 9	1	
79	Au	2	2 6	2 6 10	2 6 10 14	2 6 10	2	
80	Hg	2	2 6	2 6 10	2 6 10 14	2 6 10	2	
81	Tl	2	2 6	2 6 10	2 6 10 14	2 6 10	2 1	
82	Pb	2	2 6	2 6 10	2 6 10 14	2 6 10	2 2	
83	Bi	2	2 6	2 6 10	2 6 10 14	2 6 10	2 3	
84	Po	2	2 6	2 6 10	2 6 10 14	2 6 10	2 4	
85	—	2	2 6	2 6 10	2 6 10 14	2 6 10	2 5	
86	Rn	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	
87	—	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	1
88	Ra	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	2
89	Ac	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 1	2
90	Th	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 2	2
91	Pa	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 3	2
92	U	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 4	2

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## PROBLEMS

1. A beam of cathode rays was deflected by a magnetic field of 4.5 emu into an arc having a radius of curvature of 15 cm. An electric field of 50.0 volts per cm. was required to bring the path of the rays back to its original position (1 volt per cm. =  $10^8$  emu. per cm.)

(a) What is the velocity of the rays?

(b) If  $e = 1.59 \times 10^{-20}$  emu., calculate the mass of an electron.

*Ans.* (a)  $1.11 \times 10^9$ . (b)  $9.7 \times 10^{-28}$  g.

2. An investigation of the wavelengths of the  $K_{\alpha}$  lines in the x-ray spectra of various elements gave for zinc (atomic number 30)  $\lambda_{K_{\alpha}} = 1.445 \text{ \AA.}$  and for cobalt (atomic number 27)  $\lambda_{K_{\alpha}} = 1.798 \text{ \AA.}$  A third element showed a third-order reflection from a rock-salt crystal ( $d = 8.454 \times 10^{-8}$  cm.) at  $\theta = 36.7^{\circ}$ . What was the third element?

*Ans.* Calcium.

3. The mass spectrum of a mixture of carbon dioxide and methane gave lines which corresponded to the following ratios of mass to number of charges:

6, 8, 12, 13, 14, 15, 16, 28, 32, 44

Suggest positive ions which may be responsible for each of these lines.

4. The atomic number of phosphorus is 15.

(a) How are the fifteen electrons around the nucleus arranged in groups?

(b) Show that this distribution of electrons is in agreement with the quantum numbers and Pauli principle.

(c) How many electrons are there in the outermost group?

5. On the basis of the quantum numbers and the Pauli principle place an element having 13 electrons in its proper group in the periodic table.

6. Explain why manganese has a variable valence and bromine ordinarily does not.

7. Cite all the evidence available concerning the relative stability of elements of odd and even atomic numbers.

8. Describe the properties of element 93.



## CHAPTER XXIII

### MOLECULAR STRUCTURE

**Valence.** The combination of atoms to give a variety of molecules is of fundamental importance in all chemical reactions and biological processes. In earlier chapters the laws which govern chemical equilibrium and reaction rates have been studied and it has been seen that the course of a chemical reaction can be predicted with fair accuracy when a sufficient number of factors are known.

A simple method of presenting the facts of chemical combination is desirable. It is necessary for the chemist to know which combinations of atoms are stable and which are not. The permissible ways in which atoms can go together to form compounds have been handled in a very satisfactory manner by the simple rules of valence in which carbon is given a combining power or valence of 4, hydrogen of 1, oxygen of 2, etc. Many of the successes of chemistry and particularly organic chemistry have been due to this simple concept.

However, these valence rules are unsatisfyingly empirical, and often they are inadequate. During the past two decades important attempts have been made to put the concept of valence on a more fundamental basis and to make it more widely useful. The theory of the electron pair, the octet, and the quantum mechanical approaches have been the result. The more general and accurate theories are complicated, and one must choose between simplicity and accuracy. For ordinary purposes the older idea of valence hooks is sufficient, but the electron pair and to a limited extent the octet are useful, particularly in organic chemistry.

In attacking the problem of valence and the stability of molecules, the definition of stability should be considered. For example, a given arrangement of atoms might give a molecule accompanied by a decrease in free energy so that the change to the newer form would be theoretically spontaneous; or it might be stable because the new molecule possessed a large energy of activation and would have a long life; or it might be stable because it could not react readily with other substances with which it was in contact. For example, the free radical  $\text{CH}_3$  violates the simple rules of valence but it is a stable and perfectly legitimate molecule according to quantum mechanical calculations.

It is short-lived merely because it reacts so readily with other substances with which it is in contact. It has a large energy of activation for decomposition, but a small energy of activation for reaction with other molecules.

This second definition of stability, based on reaction rates, seems to be the best one. The arbitrariness of any definition may be emphasized, however, with just one illustration. Nitrogen pentoxide is a relatively stable substance in the arctic regions but it is unstable in the tropics. A set of valence rules which predicts the stability of nitrogen pentoxide would be satisfactory for low temperatures but not for high temperatures. At very high temperatures, of course, no organic compounds would exist and the ordinary rules of valence would not be applicable. Obviously the simpler rules of valence, the electron pair, the octet, and even the quantum numbers have nothing to do with temperature.

The electron pair or the rule of 2 emphasized by Lewis (discussed on page 9) has become established by the developments of quantum theory. As shown before, an electron can have two different spin quantum numbers and in atoms and molecules the Pauli exclusion principle demands that if all the other quantum numbers are the same these two must be different. If there is room in a given energy level for two electrons and if two electrons are available there will be a tendency for both to go into this same energy level in order to keep the energy of the system at a minimum, i.e., to keep the molecule as stable as possible. If one electron is required by the Pauli exclusion principle to seek a higher energy level an additional amount of energy must be supplied. They can both go into the same energy level (i.e., a level in which the first three quantum numbers are alike) only if their spins are opposite. One electron must have an  $m_s$  value of  $+\frac{1}{2}$  and the other a value of  $-\frac{1}{2}$ . Otherwise they would violate the Pauli principle. The pairing of electrons or combining of electrons with opposite spins is thus understood in terms of energy considerations and the Pauli principle.

The tendency of electrons to go in pairs is almost universal—so universal in fact that only a few molecules containing an odd number of valence electrons are known. When these *odd molecules* do exist, they are in fact abnormal. They tend to associate, and they are usually colored. Nitrogen dioxide and triphenylmethyl are examples.

Another point of interest is the prediction that compounds containing the same total number and arrangement of electrons have similar physical properties. Such compounds are called *isosteres*.

Carbon dioxide and nitrous oxide each have the same number, 22, of electrons arranged in the same way and are, therefore, isosteric. The freezing points are quite different, but most of the other physical properties, including critical temperature and critical pressure, dielectric constant, viscosity, refractive index, heat conductance, and surface tension, are nearly identical. The ions  $\text{NO}_3^-$  and  $\text{CO}_3^{--}$  are also isosteric, and the crystals of sodium nitrate and calcium carbonate are very similar.

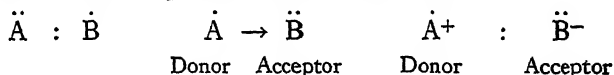
The Heitler-London theory seeks to explain molecule formation in terms of quantum numbers of the atoms out of which the molecule is formed and is more fundamental than the empirical electron pair of Lewis in that the electron pair arises from more theoretical considerations. According to it any unpaired electron left over in an atom will seek to pair off with the unpaired electron of another atom, thus forming an electron-pair bond. The number of these unpaired electrons is equal to the positive valence in terms of the classical theory of valence, but it is determined from quantum numbers in logical manner from a set of rules or postulates. The promotion of electrons to outer energy levels is possible when the energy involved is not too great, and according to the theory these "excited" atoms are of common occurrence and remain unchanged throughout many chemical changes. The energy changes are greatest in the promotion of electrons from the first to the second shell, and the energy requirement becomes progressively less in the larger shells. This fact explains the multiple valences in the heavier atoms and the lack of multiple valences among the lighter elements. The color and paramagnetism and variable valences of the transition elements titanium (22) to copper (29) and lanthanum (57) to lutecium (71) are also understandable because the transfer from outer shells to partly filled inner shells in these atoms involves comparatively small amounts of energy.

The Hund-Mulliken theory regards the molecule as consisting of nuclei and electrons rather than of atoms joined together, i.e., the molecule is formed from and can be broken down into atoms but does not *consist* of them. According to this theory\* the electrons in a molecule are to be described in terms of quantum numbers appropriate to the symmetry of the molecule. The molecule is considered to be a group of nuclei and electrons, the electrons being described in terms of molecular energy levels. According to this point of view the atoms have lost their identity in the molecule and it is meaningless to speak of the valence of nitrogen or carbon in a molecule.

\* Mulliken, *Chem. Rev.*, **9**, 349-388 (1931).

**Electron Theory of Valence.** The electron theory has been expanded in an attempt to explain the properties and chemical reactivity of molecules. Although the concepts have not been made quantitative as yet, they have been successful in correlating and predicting many chemical facts. For details and applications the literature must be consulted.\*

In general, a molecule is considered to be composed of nuclei, and electrons which come from atoms or groups which are either electron donors or electron acceptors. The important case of oxidation and reduction (oxidizing agents are electron acceptors and reducing agents are electron donors) has been fully discussed before. If an electron moves from part of a molecule to another, the fact is indicated in the structural representation of the molecule by an arrow or more frequently by writing in a plus and minus sign, thus

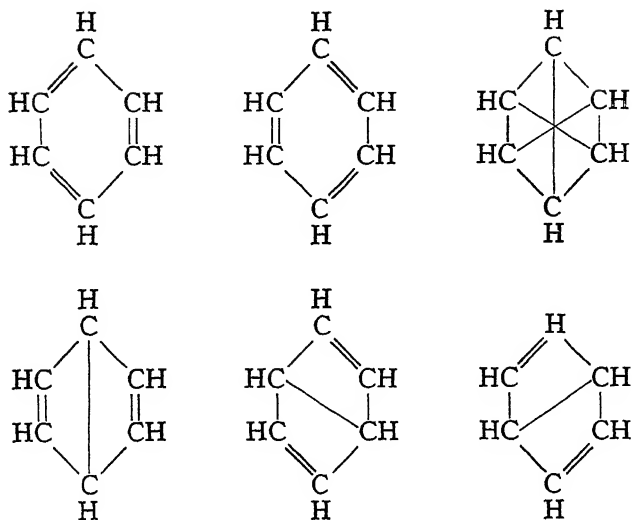


The elaborated electron theory is concerned not only with the positions of the electrical charges or *polarization*, but also with their mobility or *polarizability*. The polarization is described in part by the dipole moment  $\mu$  (page 77) and the polarizability by a coefficient  $\alpha$  which is related to the molar refraction. The polarization and polarizability of a molecule can be given roughly in terms of values assigned to pairs of atoms and atomic groups, but the influence of structure and of solvents affect the behavior also.

The organic groups and the molecules with which they react are arranged in tables in order of their ability to attract or repel electrons and a distinction is made between the position of the electrons and the ease with which they can be moved to new positions.

The concept of resonance is important and it can be measured quantitatively. Resonance exists when nuclei are arranged in a molecule so that by the rapid shifting of electrons from one position to another, two or more different structures can exist in which the energies are nearly the same. Thus there are six different ways in which the benzene structure might be drawn, thus

\* Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940; Sidgwick, "The Electron Theory of Valence," Oxford University Press, Oxford, 1929; Sidgwick, "Some Physical Properties of the Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933; Ingold, "Principles of an Electronic Theory of Organic Reactions," *Chem. Rev.*, **15**, 225 (1934); Johnson, in Gilman's "Organic Chemistry," John Wiley and Sons, New York, 1938, Chapter 19



By rapidly oscillating between the various positions, the electrons can give to benzene some of the properties expected from each of these structures. When such a situation exists, the energy of formation is increased, more energy is required to break it up, and the molecules possessing resonance have an increased stability. This fact explains why benzene and the aromatic compounds in general are so stable.

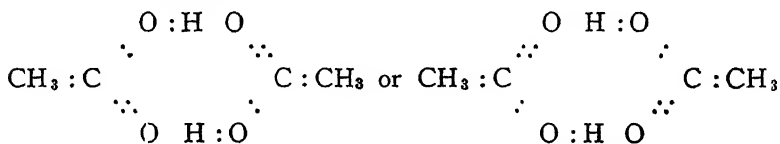
The existence of resonance and the extent of the resonance energy may be determined by comparing the heat of reaction with the normal value expected on the basis of the sum of the separate parts of the molecule. Another test for resonance is obtained by comparing the distance between atoms in the molecule with the normal interatomic distance of the bond as obtained from electron diffraction patterns (page 83). If there is resonance in a molecule, the distance between atoms in the resonance structure will be less than the normal distance found in other molecules. Molecules containing conjugated double bonds, i.e.,  $(-C=C-C=C-)$ , are particularly favorable for the rapid movement of electrons and the formation of a molecule with resonance.

Another case in which resonance is possible involves molecules with hydrogen adjacent to donor atoms. Hydrogen can have a true valence of only one, but it is abnormal in that the hydrogen ion is a proton or nucleus having a very small diameter. As such, it can penetrate structures which could not be penetrated by any other atom. Owing to this abnormality hydrogen can sometimes take up *two* pairs of electrons in a

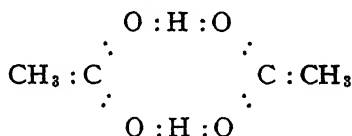
resonance structure and can give what is known as a hydrogen bond. A *hydrogen bond* is defined as an attractive force between unshielded electrons from some electron-accepting group and a proton from an electron donating group.

The particular attraction of the hydrogen bond is responsible for several phenomena of physical and organic chemistry, for example, the existence of certain maximum boiling point mixtures (page 187), certain abnormal freezing-point depressions, polymerizations, heats of mixing, shifts of infrared bands, and other phenomena.\*

As one specific example, the doubling of acetic acid molecules may be cited. The double weight can be explained on the basis that the hydrogen can share two pairs of electrons, one at a time, in a rapidly alternating electron structure thus:



the average being



This stable ring held together with two hydrogen bonds accounts for the fact that in the vapor state or in nonpolar solvents below about 150°, the acetic acid exists in double molecules. All carboxylic acids show this tendency to form double molecules.

**Electrostatic Attractions.** As already stated, electrostatic attraction is important in holding atoms together in crystals, molecules, and loose intermolecular complexes. Even in essentially homopolar bonds some of the force holding the atoms together is electrostatic in nature. Electrostatic attraction applies not only to ions but also to dipoles and induced dipoles. An ion is an atom or group of atoms with a definite electrical charge caused by the addition or removal of electrons. A dipole is a molecule in which the positive and negative charges are equal but arranged in such a way that part of the molecule is predominantly positive and another part predominantly negative so as to give an electrical unbalance. The magnitude of the total

\*Lassettre, *Chem. Rev.*, **20**, 259 (1937); Rodebush, *Chem. Rev.*, **19**, 59 (1936); Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

effect in the molecule is measured quantitatively by the dipole moment (page 80). Water is a good example of a substance which has a large dipole moment. Induced dipoles are produced by the proximity of a charged part of a neighboring molecule. They are present in most substances, but they show up more prominently in a substance like helium where the other forces are absent. Although helium has no charge and no dipole moment, it still contains a positive nucleus and a negative electron which induces a charge in a neighboring molecule. This attraction of the induced dipoles is very small in helium but is responsible for its liquefaction at very low temperature.

There are six different combinations of these three different types of electrostatic binding,\* and each can be treated mathematically in a fairly simple way by classical electrodynamics. Examples are known of each type. It must be realized that there is no sharp distinction between types and that frequently several of these interactions are involved simultaneously.

*Ion-Ion.* The attraction between sodium and chloride ions, amounting to 197,000 kg.-cal., is an example of this ionic type of binding. Ionic bindings are much stronger than most homopolar bonds. The separation of the nuclei plays an important part. Thus a hydrogen ion or a sodium ion is held much more tightly to a fluorine ion than to an iodide ion.

*Dipole-Dipole.* When two unit dipoles are aligned head-on, thus  $(+ -)(- +)$  and are 10 Å. apart in a vacuum an energy of 28.9 kcal. per mole is required to pull them apart to infinite distance. When they are surrounded by a liquid of high dielectric constant the energy required is considerably less. This dipole attraction leads to association of liquids such as water and the alcohols and polar substances. The association involves an indefinitely large number of units and is different in character from dimers such as are formed in the association of the carboxylic acid. Substances which have very low dipole moments can nevertheless possess an appreciable attraction, thus although carbon tetrachloride has a dipole moment of zero this refers to the net moment of the whole molecule; there are positive and negative parts of the C-Cl bond, i.e., bond moments, which result in the mutual attraction of C-Cl bonds on adjacent molecules.

Many of the loose chemical compounds found in mixtures of liquids are held together by this dipole interaction as, for example, in the case of some binary liquid systems which show a departure from

\* Moelwyn-Hughes and Sherman, *J. Chem. Soc.*, 101 (1936); Moelwyn-Hughes, "Physical Chemistry," Cambridge University Press, Cambridge, 1940, pp. 92-103.

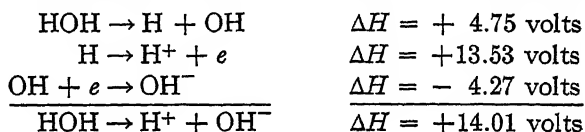
ideal behavior and exhibit curves which are not directly proportional to mole fraction. The heat of mixing in these cases is of the magnitude predicted by calculations of this dipole-dipole attraction.

The force of attraction in water is so great that 9700 cal. per mole must be introduced in order to separate the molecules in liquid water and remove them to infinite distance.

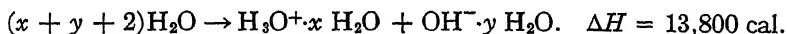
*Induced Dipole-Induced Dipole.* Although quite general, this type of attraction is frequently so small in comparison with the other types of attractions that it is unnoticed. In helium it is 25 cal. per mole and in krypton it is 2240 cal.

*Ion-Dipole.* This type of attraction is very important because it is responsible for the solubility of electrolytes in water. The following calculations are instructive.

The heat of neutralization of water is 13,800 cal. or 0.6 electron volt. However, the following reactions in the gas phase are accurately known.

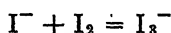


The total reaction heat of 14 electron volts corresponds to 330,000 cal. Hence the neutralization reaction which is known to evolve 13,800, cal. cannot be the reaction just written. The energy of activation required for this reaction must be at least as great as the 330,000 cal., and the reaction cannot be made to go with the expenditure of only 13,800 cal. The ordinary heat of neutralization measured in a calorimeter must involve a different reaction. It is concerned with the reaction



which involves hydrated ions. The difference between 330,000 and 13,800, namely 316,200, is the sum of the heats of hydration of the hydrogen and hydroxyl ions.

*Ion-Induced Dipole.* Certain complex ions are produced by the attractive force existing between an ion and a dipole induced in a neighboring molecule. In the reaction



part at least of the energy of combination is due to this ion-induced dipole attraction.

*Dipole-Induced Dipole.* The solubility of helium and the rare gases in water is due to this type of attraction. If there were no attraction



between helium and water there would be no reason to expect a greater concentration of the gas in the water phase than in the gas phase above it. In fact, there is evidence for the formation of an argon hydrate; and a crystalline hydrate of butane is known.

It is possible to treat these electrical attractive forces semi-quantitatively as well as qualitatively, using simple formulas which involve distance apart of the two attracting units, dielectric constant of the solvent, atomic number, dipole moment, and polarizability.

**Statistical Thermodynamics.\*** Gibbs, Boltzmann, and others applied the method of statistical mechanics to the calculation of specific heats and other thermodynamic quantities but the calculations did not agree with the experimental values. As explained earlier in this book it was necessary to wait for the development of the quantum theory before correct calculations could be made. It is now possible to calculate thermodynamic functions  $E$ ,  $S$ ,  $A$ ,  $F$ ,  $C_p$ , and  $C_v$  for many simple molecules more accurately than they can be determined by direct experimental measurements. The treatment of more complicated molecules is still rather approximate, but important progress is being made.†

The general principles involved in the application of statistical mechanics to physical chemical problems may be illustrated with the help of a simplified hypothetical system consisting of molecules in the energy state  $A$  and molecules in the energy state  $B$ , which are in equilibrium with each other; thus,



Then  $\Delta F = -RT \ln K = -RT \ln \frac{n_B}{n_A}$  where  $n_A$  and  $n_B$  are the numbers of molecules in the two states under these equilibrium conditions. For the sake of simplicity, it will be assumed that the energy in the  $A$  state is effectively zero, i.e., it is in the ground state.

Writing in the exponential form and remembering that  $\Delta F = \Delta H - T\Delta S$

$$\frac{n_B}{n_A} = e^{-\Delta F/RT} = e^{\Delta S/R} e^{-\Delta H/RT} \quad [1]$$

For this simple, hypothetical system, it is assumed that there are no energy levels other than those found in the states  $A$  and  $B$ , and so

\* Eyring and Walter, *J. Chem. Education*, **18**, 73 (1941); Wilson, *Chem. Rev.*, **27**, 17 (1940)

† Pitzer, *Chem. Rev.*, **27**, 39 (1940); Wenner, "Thermochemical Calculations," McGraw-Hill Book Co., New York, 1941, Chapters VII and VIII.

here is no way in which heat can be taken up by raising the temperature, and the heat capacities and entropies of the separate molecules in the  $A$  state and  $B$  state are equal to zero. However, there may be several different states in which all the molecules have the same energy level. Such a system is said to be degenerate and the degeneracy  $g$  is defined as the number of different states: 1, 2, 3, etc., which have the same energy content. Now these molecules of different configuration but equal energy content are uniformly mixed together in what may be considered as an ideal solution and an "entropy of mixing"  $\Delta S_m$  is involved, which is given by the expression

$$\Delta S = R \ln g^* \quad [2]$$

Substituting the value for entropy change  $\Delta S$  in going from the  $A$  state to the  $B$  state,

$$e^{\Delta S/R} = e^{(R \ln g_B - R \ln g_A)/R} = \frac{g_B}{g_A}$$

Then

$$\frac{n_B}{n_A} = \frac{g_B}{g_A} e^{-\Delta H/RT} \quad [3]$$

where  $\Delta H$  is the heat absorbed in going from the  $B$  state to the  $A$  state. Then substituting molecular quantities for molar quantities

$$\frac{n_B}{n_A} = \frac{g_B}{g_A} e^{-\epsilon_B/kT}$$

where  $\epsilon_B/kT$  is obtained from  $\Delta H/RT$  by dividing through by Avogadro's number.

\* This equation is derived as follows:

It was shown on page 220 in equation (26) that the free energy of transferring a substance from the pure state to an ideal solution is given by the expression

$$\Delta F = RT \ln N$$

where  $N$  is the mole fraction in solution. When several different substances comprise the solution

$$\Delta F = RTN_1 \ln N_1 + RTN_2 \ln N_2 + RTN_3 \ln N_3 + \dots$$

but  $\Delta S = \frac{\Delta H - \Delta F}{T}$ ; and for ideal solutions  $\Delta H = 0$ .

Then  $\Delta S = -R(N_1 \ln N_1 + N_2 \ln N_2 + N_3 \ln N_3 + \dots)$ .

In this system  $N_1 = N_2 = N_3$ , since it is assumed that all energy states are equally probable.

Then  $\Delta S = -RgN_1 \ln N_1$  and since

$$gN_1 = 1 \quad \text{and} \quad \frac{1}{N_1} = g$$

$$\Delta S = R \ln g$$

It is evident that if a third state  $C$  were specified, the same formula would apply with subscript  $C$  taking the place of subscript  $B$ . In general,

$$\frac{n_i}{n_0} = \frac{g_i}{g_0} e^{-\epsilon_i/kT} \quad [4]$$

where  $n_0$  and  $g_0$  emphasize that the first state is the ground state and  $i$  represents any state. The number  $g_i$  gives the a priori probability or the statistical weight of the energy state  $i$ .

These equations are known as the Maxwell-Boltzmann equations which constitute a theoretical foundation for many of the formulas which have been discussed in earlier chapters dealing with the influence of temperature on chemical equilibrium, solubility, vapor pressure, reaction rates, etc. They can be derived also by statistical mechanics without the use of physical chemical formulas. According to one method a system of harmonic oscillators is used as the starting point.

Rearranging equation (4)

$$n_i = \left(\frac{n_0}{g_0}\right) g_i e^{-\epsilon_i/kT}$$

The sum of the numbers of molecules in all the states must equal the total number of molecules; hence for a system of  $N$  molecules

$$N = \sum_i n_i = \left(\frac{n_0}{g_0}\right) \sum_i g_i e^{-\epsilon_i/kT}$$

Now the total energy of the  $N$  molecules in excess of the energy in the ground state (approximately at absolute zero) is given by the expression

$$\begin{aligned} E_i^0 - E_0^0 &= \sum_i \epsilon_i n_i = \left(\frac{n_0}{g_0}\right) \sum_i \epsilon_i g_i e^{-\epsilon_i/kT} \\ &= N \left( \frac{\sum_i \epsilon_i g_i e^{-\epsilon_i/kT}}{\sum_i g_i e^{-\epsilon_i/kT}} \right) \end{aligned} \quad [5]$$

where  $E_0^0$  is the energy of formation per mole of the molecules from gaseous atoms at absolute zero. These formulas may be written more simply if we use a function known as the *partition function*, defined as

$$Q = \sum_i g_i e^{-\epsilon_i/kT}$$

Then it follows that

$$n_i = \frac{N}{Q} g_i e^{-\epsilon_i/kT} \quad [6]$$

and

$$\begin{aligned}\frac{-(E^0 - E_0^0)}{T} &= \left(\frac{N}{Q}\right) \sum_i g_i \epsilon_i e^{-\epsilon_i/kT} \\ &= \left(\frac{N}{Q}\right) kT^2 \frac{dQ}{dT} = RT^2 \frac{d \ln Q}{dT}\end{aligned}\quad [7]$$

Similar analytical expressions may be obtained

$$C_v = \frac{dE}{dT} = -R \frac{d}{dT} \left( \frac{d \ln Q}{d(1/T)} \right) \quad [8]$$

$$S = R \left( \ln Q + T \frac{d \ln Q}{dT} \right) \quad [9]$$

$$\frac{-(F - E^0)}{T} = R (\ln Q - 1) \quad [10]$$

These formulas giving the thermodynamic quantities in terms of the function  $Q$  are of value because of the fact that analytic expressions can usually be found for  $Q$  which avoid the necessity of tedious summations. Spectroscopic evidence indicates that we may usually break up the energy of a given level,  $\epsilon_i$ , into separate parts (page 569), writing

$$\epsilon_i = \epsilon_{tr} + \epsilon_{el} + \epsilon_v + \epsilon_r \quad [11]$$

where these components are the translational, electronic, vibrational, and rotational energies, respectively. From the exponential nature of the partition function, it follows that we may write  $Q$  as a product of corresponding component partition functions:

$$Q = Q_{tr} \times Q_{el} \times Q_v \times Q_r \quad [12]$$

The thermodynamic functions themselves involve the logarithm of the partition function, and may therefore be broken up into sums; e.g., the entropy may be written

$$S = S_{tr} + S_{el} + S_v + S_r \quad [13]$$

It is found that in almost all cases the electronic energy levels lie so high that only a negligible fraction of the molecules are electronically excited by thermal agitation, and hence the electronic contributions may usually be ignored. The vibrational contributions are evaluated by summation. The translational and rotational contributions may be closely approximated, at ordinary temperatures, by analytic functions of the molecular weight, and by moments of inertia of the molecule.

Tables are now available giving values of  $\frac{-(F^0 - E_0^0)}{T}$  at various

temperatures for many of the hydrocarbons and simple molecules.\*

Using these values together with one experimental value in order to calculate  $\Delta E_0^0$  one can calculate  $\Delta F^0$  and thus the chemical equilibrium constant using the relation  $-\Delta F^0 = RT \ln K$ .

**Calculation of Activation Energies.** It is to be hoped that theoretical chemistry will provide a means of calculating from a few fundamental constants not only the thermodynamical quantities and equilibrium constants as just described but energies of activation and reaction rates as well. A beginning has been made. However, so many more variables are involved, such as time, catalysts, foreign materials, and light, that the developments will be much slower and the results will be subject to much greater errors. Moreover, in thermodynamics one can handle and measure the substances involved, but in chemical kinetics many of the most important substances have only a fleeting existence and cannot be investigated by direct methods. However, from a practical standpoint the prediction of reaction rates is so important that even approximate results are welcome.

The importance of the activation energy  $E$  and its use in calculating reaction rates with the formula

$$k = se^{-\Delta H_a/RT} \quad [14]$$

were stressed in Chapter XIV. If one could place all the atoms involved in a given reaction at all different positions in space and determine the energy of the system at all these different spacings he would then know the most stable products and the energies required to bring up the reactants into such positions that the given products would result. The problem is complicated because every atom interacts with every other atom and because, as already explained, there are both electrostatic and quantum mechanical attractions.

The problem has been attacked by Eyring.† It is *assumed* that the atom pairs retain their individuality until they reach such a configuration that the atoms can either return to give the original molecule or rearrange to give the new products. The general plan is to build up curves giving energies as a function of distance for all the different atom pairs and arrange them in three dimensions with energies plotted vertically from a basal plane. Theoretically, these curves can be built up from quantum numbers and spectroscopic constants when these

\* Pitzer, *Chem. Rev.*, **27**, 39 (1940); Wilson, *Chem. Rev.*, **27**, 17 (1940); Wenner, "Thermochemical Calculations," McGraw-Hill Book Co., New York, 1941; Johnston and Davis, *J. Am. Chem. Soc.*, **56**, 271 (1934).

† Eyring, *Chem. Rev.*, **10**, 103 (1932); Glasstone, Laidler, and Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, 1941.

are known sufficiently well. In the absence of these more complete data, Morse curves are used as described on page 570, and in calculating them it is necessary to know three things: the vibration frequencies of the atoms, the interatomic distances in the normal molecule, and the heats of dissociation. These constants are now available for several atom pairs.

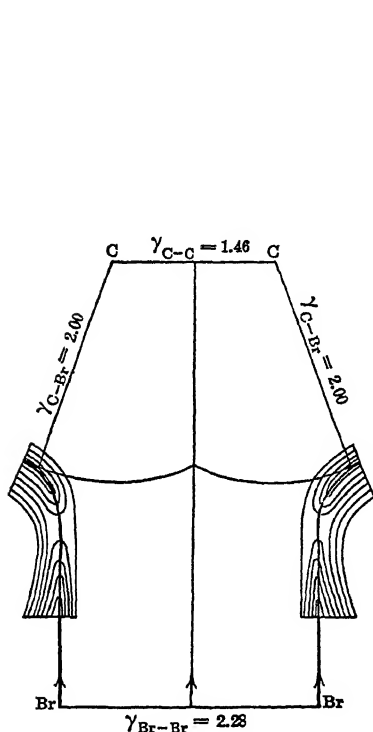


FIG. 165

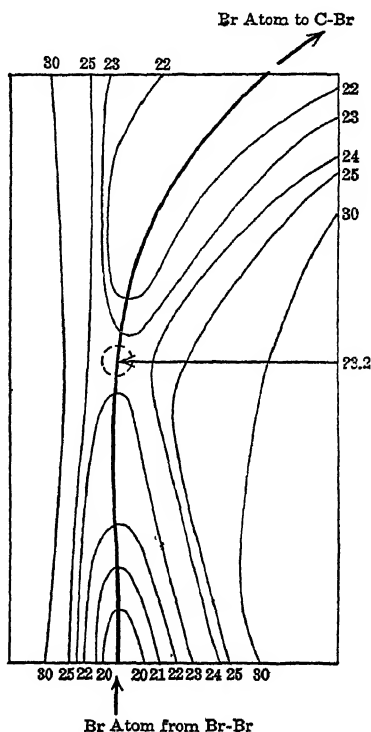


FIG. 166

Energy contours are built up by solving the complicated equations which allow for the mutual interactions between all the atoms, and the object is to find the least amount of energy which can be supplied to push the atoms from their stable positions in the reactants to their stable positions in the products. In other words, the lowest mountain pass separating two valleys in an energy contour map is sought, and the height of this pass is the energy of activation.

Such an energy contour map is shown in Fig. 166 for the addition of bromine to the double bond of an unsaturated organic compound. The two bromine atoms in the stable bromine molecule rest in energy val-

leys running vertically on the page. As they come up close to the carbon-carbon double bond the old forces of attraction are altered and the new ones are formed. After going over an energy hill at the lowest possible point they settle down into low-energy valleys again in a stable carbon-bromine compound. The routine calculations are reduced because the only object is to find the minimum energy required, and rough estimates are adequate for most of the map; special care and frequent calculations are necessary only in the region of the pass separating the two valleys. An enlarged scale of this region is shown in Fig. 166. The approximations necessary to give practical solutions for calculating these energy contours are so great that the method is not yet satisfactory.

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### PROBLEMS

1. Write the following structures in terms of the electron theory of valence: (a) Perchlorate ion  $\text{ClO}_4^-$ ; (b) sulfate ion  $\text{SO}_4^{--}$ ; (c) phosphate ion  $\text{PO}_4^{---}$ ; (d) cupric ammonium ion  $\text{Cu}^{++} \cdot 4\text{NH}_3$ .

2. Write the following reaction in terms of the electron theory of valence: (a)  $\text{Fe}^{++} \rightarrow \text{Fe}^{+++} + e$ ; (b)  $\text{Zn} + \text{S} \rightarrow \text{ZnS}$ ; (c)  $\text{C}_2\text{H}_4 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_4\text{Cl}_2$ ; (d)  $\text{C}_2\text{H}_6 + 2\text{Cl}_2 \rightarrow \text{C}_2\text{H}_4\text{Cl}_2 + 2\text{HCl}$ .

3. Represent the following chemical compounds on the basis of the electron theory of valence: (a)  $\text{H}_2$ ; (b)  $\text{LiH}$ ; (c)  $\text{CH}_4$ ; (d)  $\text{HCl}$ ; (e)  $\text{Cl}_2$ .

4. Give illustrations of the various interactions involving ions, dipoles, and induced dipoles.

5. Hydrofluoric acid is unique as a solvent. On the basis of the small radius and low atomic number, state what abnormal solvent properties one might expect to find in hydrofluoric acid.

6. (a) Develop a system of valence rules for a temperature of  $1000^\circ$ .

(b) Develop a system of valence rules for a temperature of  $-100^\circ$ .

7. At  $50^\circ$  the vapor pressures of *o*-xylene, *m*-xylene and *p*-xylene are respectively 25.1, 29.3, and 32.3 mm. Explain qualitatively on the basis of molecular structure and interactions between molecules why these vapor pressures should be related to each other in this way.

## APPENDIX

### Table of Physical Chemical Constants\*

Approximate values of some of these constants are given also on page xii.

One liter (1000 ml.)	1000.028 cm. <sup>3</sup>
Standard acceleration of gravity	980.665 cm. sec. <sup>-2</sup>
Standard atmosphere	$1.013246 \times 10^6$ dynes cm. <sup>-2</sup>
Volume of perfect gas at 0° C., 1 standard atmosphere	22.4140 liters mole <sup>-1</sup>
Ice point (0° C.)	273.16° K.
One calorie (defined)	4.1833 international joules
One 15° calorie	4.1847 international joules
Gas constant per mole	$8.3144 \times 10^7$ ergs. deg. <sup>-1</sup> mole <sup>-1</sup> 1.98711 cal. deg. <sup>-1</sup> mole <sup>-1</sup> 0.082,054 liter-atm. deg. <sup>-1</sup> mole <sup>-1</sup>
One international ohm	1.00048 absolute ohm
One international ampere	0.99986 absolute amp.
One international joule	1.00020 absolute joule
Faraday constant	96501 international-coulomb gram-equivalent <sup>-1</sup>
Avogadro number	$6.023 \times 10^{23}$ mole <sup>-1</sup>
Electronic charge	$1.6020 \times 10^{-20}$ absolute emu. $4.8025 \times 10^{-10}$ absolute esu.
Mass of electron	$9.107 \times 10^{-28}$ g.
Rydberg constant for H <sup>1</sup>	109677.58 cm. <sup>-1</sup>
Rydberg constant for He <sup>4</sup>	109722.26 cm. <sup>-1</sup>
Rydberg constant for infinite mass	109737.30 cm. <sup>-1</sup>
Planck's constant	$6.624 \times 10^{-27}$ erg. sec.
One absolute volt-electron	$1.6020 \times 10^{-12}$ erg. molecule <sup>-1</sup> 23,060 cal. mole <sup>-1</sup>
Boltzmann constant (gas constant per molecule)	$1.3805 \times 10^{-16}$ erg. deg. <sup>-1</sup> molecule <sup>-1</sup>
One kilocalorie mole <sup>-1</sup>	$6.9482 \times 10^{-14}$ erg molecule <sup>-1</sup> = 0.043374 electron volt = 349.93 cm. <sup>-1</sup> (wave numbers)

\* R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941). Constants given in calories have been recalculated in terms of the defined calorie.



## Mathematical Formulas\*

## CALCULUS

$\Delta$  = small finite increment;  $d$  = differential;  $dy/dx$  = derivative = limit of  $\Delta y/\Delta x$  as  $\Delta x$  approaches zero

$$y = x^n; \quad dy/dx = nx^{n-1}$$

$$y = f_1(x) + f_2(x); \quad dy/dx = \frac{df_1(x)}{dx} + \frac{df_2(x)}{dx}$$

$$y = k; \quad dy/dx = 0$$

$$y = kf(x); \quad dy/dx = k \frac{df(x)}{dx}$$

$$y = uv; \quad dy/dx = u \, dv/dx + v \, du/dx$$

$$y = u/v; \quad dy/dx = \frac{v \, du/dx - u \, dv/dx}{v^2}$$

$$y = e^x; \quad dy/dx = e^x$$

$$y = \log_e x; \quad dy/dx = 1/x$$

$$y = \log x; \quad dy/dx = 0.4343/x$$

$$y = \log_a x; \quad dy/dx = \frac{\log_a e}{x}$$

$$y = a^x; \quad dy/dx = a^x \log_e a$$

$$y = f_2[f_1(x)]; \quad dy/dx = \frac{df_2[f_1(x)]}{df_1(x)} \times \frac{df_1(x)}{dx}$$

For a maximum or minimum or point of horizontal inflection,  $dy/dx = 0$ .

For a differential,  $dy = (dy/dx) \, dx$ .

For partial differentiation where  $u = f(x, y, z)$

$$du = \left( \frac{\partial u}{\partial x} \right)_{y, z} dx + \left( \frac{\partial u}{\partial y} \right)_{x, z} dy + \left( \frac{\partial u}{\partial z} \right)_{x, y} dz$$

$$\int dx = x + C$$

$$\int x^n dx = x^{n+1}/(n+1) + C$$

$$\int x^{-1} dx = \log_e x + C$$

$$\int kf(x) dx = k \int f(x) dx$$

$$\int [f_1(x) + f_2(x) + f_3(x)] dx = \int f_1(x) dx + \int f_2(x) dx + \int f_3(x) dx$$

$$\int [k + f(x)] dx = \int k dx + \int f(x) dx = kx + \int f(x) dx + C$$

$$\int e^x dx = e^x + C$$

\* An elementary treatment of the mathematics needed for the study of physical chemistry is given by Daniels, "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., New York, 1928.

$$\int a^x dx = \frac{a^x}{\log_e a} + C$$

$$\int \log_e x dx = x (\log_e x - 1) + C$$

$$\int \log x dx = 0.4343 x (\log x - 1) + C$$

$$\int \log_a x dx = (\log_a e)(x)(\log_e x - 1) + C$$

$$\text{Integrating between limits } \int_a^b x dx = \left[ \frac{x^2}{2} \right]_a^b = \frac{b^2}{2} - \frac{a^2}{2}$$

## TRIGONOMETRY

sine = ordinate/hypotenuse

cosine = abscissa/hypotenuse

tangent = ordinate/abscissa

$1^\circ = 0.0175$  radian

$\sin^2 x + \cos^2 x = 1$

$y = \sin x; dy/dx = \cos x$

$y = \cos x; dy/dx = -\sin x$

$y = \tan x; dy/dx = \sec^2 x$

$$\int \sin x dx = -\cos x + C$$

$$\int \cos x dx = \sin x + C$$

## MISCELLANEOUS

$$\text{If } ax^2 + bx + c = 0, \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

1 inch = 2.54 cm.    1 pound = 453.6 g.

log means  $\log_{10}$ ;    ln means  $\log_e$ .

## Greek Alphabet

A $\alpha$	Alpha	N $\nu$	Nu
B $\beta$	Beta	Ξ $\xi$	Xi
Γ $\gamma$	Gamma	Ο $\omicron$	Omicron
Δ $\delta$	Delta	Π $\pi$	Pi
E $\epsilon$	Epsilon	Ρ $\rho$	Rho
Z $\zeta$	Zeta	Σ $\sigma$	Sigma
H $\eta$	Eta	Τ $\tau$	Tau
Θ $\theta$	Theta	Υ $\upsilon$	Upsilon
I $\iota$	Iota	Φ $\phi$	Phi
K $\kappa$	Kappa	Χ $\chi$	Chi
Λ $\lambda$	Lambda	Ψ $\psi$	Psi
M $\mu$	Mu	Ω $\omega$	Omega

A few of the more specialized and technical formulas are derived in this section of the book. The page number on which the formula occurs is given in each case.

### Evaluation of van der Waals' Constants $a$ and $b$

(Page 25)

The three roots of van der Waals' equation become equal at the critical temperature where  $B$ ,  $C$ , and  $D$  unite in a point as shown in Fig. 8. Then

$$v^3 - \left(b + \frac{RT_c}{p_c}\right)v^2 + \frac{a}{p_c}v - \frac{ab}{p_c} = 0 \quad [1]$$

where the subscript  $c$  indicates the critical state and the three roots  $v_1 = v_2 = v_3$  are all equal to  $v_c$ . Then  $v - v_c = 0$  and  $(v - v_c)^3 = 0$ . Expanding by the binomial theorem

$$(v - v_c)^3 = v^3 - 3v_c v^2 + 3v_c^2 v - v_c^3 = 0 \quad [2]$$

Equating the coefficients of  $v$  in (1) and (2)

$$3v_c^2 = \frac{a}{p_c} \quad [3]$$

and equating the constant terms

$$v_c^3 = \frac{ab}{p_c} \quad [4]$$

It is possible then to determine the values of the constants  $a$  and  $b$  for any gas from a knowledge of the critical volume and critical pressures, thus

$$a = 3p_c v_c^3 \quad [5]$$

Dividing equation (4) by equation (3)

$$b = \frac{v_c}{3} \quad [6]$$

Equating the coefficients of  $v^3$  in a similar manner and substituting the values of  $v_c$  and  $p_c$  it can be shown that

$$R = \frac{8}{3} \frac{p_c v_c}{T_c} \quad [7]$$

Obviously  $a$ ,  $b$ , and  $R$  must be expressed in the same units as  $p$  and  $v$ . It is customary to express  $a$  in atmospheres  $\times$  milliliters and  $b$  in milliliters.

### The Beattie-Bridgman Equation of State

(Page 28)

The Beattie-Bridgman\* equation is

$$p = \frac{RT}{V^2} \left[ V + B_0 \left( 1 - \frac{b}{V} \right) \right] \left[ 1 - \frac{c}{VT^3} \right] - \frac{A_0}{V^2} \left( 1 + \frac{a}{V} \right)$$

The five constants must be evaluated from experimental data on each gas. They are recorded in the literature for a few of the common gases. For carbon dioxide,

\* Beattie and Bridgman, *J. Am. Chem. Soc.*, **49**, 1665 (1927); **50**, 3133 (1928).

the constants are  $A_0 = 5.0065$ ;  $B_0 = 0.10476$ ;  $a = 0.07132$ ;  $b = 0.07235$ ;  $c = 6.60 \times 10^5$ . The equation may be illustrated by calculating the pressure,  $p$ , exerted by a mole of carbon dioxide at  $50.00^\circ$  in a given volume.

$$p = \frac{0.08206 \times 323.15}{V^2} \left[ V + 0.10476 \left( 1 - \frac{0.07235}{V} \right) \right] \left[ 1 - \frac{6.60 \times 10^5}{V(323.15)^3} \right] - \frac{5.0065}{V^2} \left( 1 - \frac{0.7132}{V} \right)$$

When  $V = 0.300$  liter

$$\begin{aligned} p &= 294.66 (0.300 + 0.079495)(0.9348) - 55.63 (0.76227) \\ &= 104.53 - 42.41 = 62.12 \text{ atm.} \end{aligned}$$

### Distance between 111 Planes

(Page 47)

$$d_{111} = \frac{1}{\sqrt{3}}$$

In Fig. 16c or 17c three 111 planes are shown and the vertical distance between any two of them is to be calculated. Running from the origin (i.e. the central point in the lowest central line), one finds the oblique line ending in an arrow, at right angles to the plane. This is the distance  $d$  which is sought.

If the line is continued until it hits the upper right-hand corner it forms a diagonal of the cube. Geometrical considerations show that the diagonal of the cube will intersect the planes at right angles.

Now the length  $l$  of the diagonal of a cube is given by the expression

$$l^2 = x^2 + y^2 + z^2 \quad [1]$$

where  $x$ ,  $y$ , and  $z$  are the three sides of the cube. But, by definition of the 111 plane

$$x = y = z = 1 \quad [2]$$

since the plane cuts each of the three axes at a distance of unity.

Then

$$l^2 = x^2 + y^2 + z^2 = 1^2 + 1^2 + 1^2 = 3 \quad [3]$$

By inspection of these figures it is evident that the diagonal is divided into three sections by these three parallel, 111 planes. When other cubes are laid down around these cubes it can be seen from the intersection on the upper faces that the 111 planes are parallel and separated by constant differences.

Then the distance  $d$  between the two planes, or in fact between any two planes, is given by the relation

$$d = \frac{1}{3}l = \frac{1}{3}\sqrt{3} \quad [4]$$

or

$$d_{111} = \frac{1}{\sqrt{3}} \quad [5]$$

### Calculation of Refractive Index from Angle of Refraction

(Page 61)

The light passes through the (Pulfrich) refractometer prism as shown in Fig. 167.

The refractive index  $n$  at the air-liquid interface may be obtained from the refractive index  $N$  at the air-glass interface and the refractive index  $n_1$  at the liquid-glass

interface. Dividing  $N$  by  $n_1$  the refraction in glass can be made to disappear. Therefore

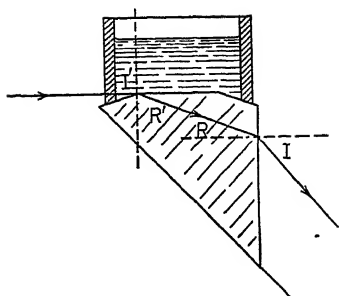


FIG 167

$$n = \frac{N}{n_1} = \frac{N}{\sin I' / \sin R'} \quad [1]$$

But  $I' = 90^\circ$ , and  $\sin I' = 1$ ,

$$n = \frac{N}{1/\sin R'} = N \sin R' \quad [2]$$

and since  $\sin R' = \cos R = \sqrt{1 - \sin^2 R}$

$$n = N \sqrt{1 - \sin^2 R} \quad [3]$$

For air-glass,

$$N = \frac{\sin I}{\sin R}; \text{ or } \sin^2 R = \frac{\sin^2 I}{N^2} \quad [4]$$

and substituting,

$$n = N \sqrt{1 - \frac{\sin^2 I}{N^2}} = \sqrt{N^2 - \sin^2 I} \quad [5]$$

The value of the refractive index  $N$  of the glass prism against air is supplied with the refractometer.

### Partial Differentiation

(Page 99)

The fundamental formula of partial differentiation is that if  $u$  is a function of both  $x$  and  $y$  then

$$du = \left( \frac{\partial u}{\partial x} \right)_y dx + \left( \frac{\partial u}{\partial y} \right)_x dy \quad [1]$$

Applying it to the specific example of a perfect gas, it is evident that the volume  $v$  of the gas is a function of both temperature  $T$  and pressure  $p$ . Each of these variables affects the volume independently of the other. Then

$$dv = \left( \frac{\partial v}{\partial T} \right)_p dT + \left( \frac{\partial v}{\partial p} \right)_T dp \quad [2]$$

This equation may be expressed in words as follows. The slight change in the volume of a gas, produced by changing the temperature and pressure simultaneously, is equal to the sum of two quantities: (1) the change in temperature multiplied by the rate at which volume changes with temperature, and (2) the change in pressure multiplied by the rate at which volume changes with pressure.

The method of partial differentiation may be illustrated in the following proof that

$$C_p - C_v = R \quad [3]$$

This equation was developed in a different way on page 104. The molar heat capacity at constant pressure  $C_p$  is defined as the rate of change of heat content with temperature at constant pressure. The molar heat capacity at constant volume  $C_v$  is

defined as the rate of change of internal energy  $E$  with temperature at constant volume.

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad \text{and} \quad C_v = \left( \frac{\partial E}{\partial T} \right)_v \quad [4]$$

Therefore

$$\begin{aligned} C_p - C_v &= \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial E}{\partial T} \right)_v \\ &= \left[ \frac{\partial(E + pv)}{\partial T} \right]_p - \left( \frac{\partial E}{\partial T} \right)_v \\ &= \left( \frac{\partial E}{\partial T} \right)_p + p \left( \frac{\partial v}{\partial T} \right)_p - \left( \frac{\partial E}{\partial T} \right)_v \end{aligned} \quad [5]$$

But since  $E$  is a single-valued function of the variables  $T$  and  $v$ , it follows that

$$dE = \left( \frac{\partial E}{\partial T} \right)_v dT + \left( \frac{\partial E}{\partial v} \right)_T dv \quad [6]$$

and differentiating with respect to  $T$  at constant pressure,

$$\left( \frac{\partial E}{\partial T} \right)_p = \left( \frac{\partial E}{\partial T} \right)_v + \left( \frac{\partial E}{\partial v} \right)_T \left( \frac{\partial v}{\partial T} \right)_p \quad [7]$$

Substituting in equation (5) we obtain

$$C_p - C_v = \left( \frac{\partial E}{\partial T} \right)_v + \left( \frac{\partial E}{\partial v} \right)_T \left( \frac{\partial v}{\partial T} \right)_p + p \left( \frac{\partial v}{\partial T} \right)_p - \left( \frac{\partial E}{\partial T} \right)_v \quad [8]$$

But for a perfect gas  $\left( \frac{\partial E}{\partial v} \right)_T = 0$  (page 101). Hence equation (8) becomes

$$C_p - C_v = p \left( \frac{\partial v}{\partial T} \right)_p \quad [9]$$

and since  $v = \frac{RT}{p}$ , we may replace  $\left( \frac{\partial v}{\partial T} \right)_p$  by  $\frac{R}{p}$ , and equation (9) then simplifies to

$$C_p - C_v = R \quad [10]$$

The use of partial differentiation may be illustrated further in the study of the Joule-Thomson effect discussed on page 102.

Since  $H$  is a single-valued function of any two of the three variables  $T$ ,  $p$ , and  $v$ , the general rule for partial differentiation may be applied; choosing temperature and pressure as the variables, we may write

$$dH = \left( \frac{\partial H}{\partial T} \right)_p dT + \left( \frac{\partial H}{\partial p} \right)_T dp \quad [11]$$

But in case of the free expansion of gas,  $H$  is constant and  $dH = 0$ , so that on rearranging terms

$$\left( \frac{\partial T}{\partial p} \right)_H = \frac{-\left( \frac{\partial H}{\partial p} \right)_T}{\left( \frac{\partial H}{\partial T} \right)_p} = \frac{-\left( \frac{\partial H}{\partial p} \right)_T}{C_p} \quad [12]$$

Writing for  $H$  its equivalent  $E + pv$

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{-\left(\frac{\partial(E + pv)}{\partial p}\right)_T}{C_p} = -\frac{1}{C_p}\left(\frac{\partial E}{\partial p}\right)_T - \frac{1}{C_p}\left(\frac{\partial(pv)}{\partial p}\right)_T \quad [13]$$

In this equation  $-\frac{\partial E}{\partial p}$  corresponds to the decrease in internal energy as the molecules are crowded closer together, a process which liberates heat and causes the temperature to rise if the system is thermally insulated. According to this term a decrease in pressure should produce a drop in the temperature.

Neglecting the term  $-\frac{1}{C_p}\left(\frac{\partial E}{\partial p}\right)_T$  and considering only the last term of the equation, if  $pv$  increases when  $p$  decreases  $\frac{dT}{dp}$  will have a positive value and the gas will tend to be cooled when the pressure is decreased by the passage of the gas through a porous plug. If  $pv$  decreases when  $p$  decreases  $\frac{\partial(pv)}{\partial p}$  will be positive and  $\frac{dT}{dp}$  will be negative indicating that the temperature will rise.

### The Carnot Cycle

(Page 141)

The Carnot cycle makes use of an imaginary engine operating through a reversible cycle as indicated in Fig. 168. One mole of a perfect, monatomic gas is enclosed in a cylinder with a weightless, frictionless piston and subjected to the following four successive steps.

1.  $AB$  represents isothermal, reversible expansion from  $v_A$  to  $v_B$  at temperature  $T_2$ .

$$w_{AB} = \text{area } ABFG = RT_2 \ln v_B/v_A$$

$$q_{AB} = w_{AB} \quad [1]$$

2.  $BC$  represents adiabatic expansion from  $v_B$  to  $v_C$ . The temperature drops from  $T_2$  to the lower temperature  $T_1$ . No heat is transferred, and the energy for doing the work must come from the cooling of the gas,  $\Delta E$ .

$$q_{BC} = 0$$

$$w_{BC} = \text{area } BCKF = C_v(T_2 - T_1) \quad [2]$$

also

$$C_v \ln \frac{T_1}{T_2} = -R \ln \frac{v_C}{v_B} \quad (\text{adiabatic expansion}) \quad [3]$$

3.  $CD$  represents isothermal, reversible compression from  $v_C$  to  $v_D$  at temperature  $T_1$ .

$$w_{CD} = \text{area } CDHK = RT_1 \ln v_D/v_C$$

$$w_{CD} = q_{CD} \quad [4]$$

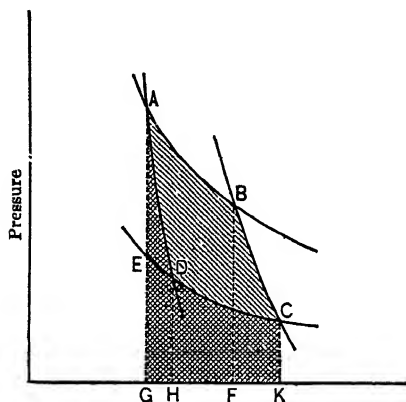


FIG. 168

4.  $DA$  represents adiabatic compression from  $v_D$  to  $v_A$ . The temperature rises from  $T_1$  to  $T_2$ .

$$q_{DA} = 0$$

$$w_{DA} = \text{area } DAGH = C_v(T_1 - T_2) = -C_v(T_2 - T_1) \quad [5]$$

also

$$C_v \ln T_2/T_1 = -R \ln v_A/v_D \quad [6]$$

The gas is now at its starting point under the original conditions of temperature, pressure, and volume, and the four steps constitute a reversible cycle. Work done by the system,  $w$ , is shaded upward from left to right, and work done on the system by its surroundings is shaded downward from right to left. More work is obtained at the higher temperature than is required at the lower temperature, and the net work is represented by the area  $ABCD$ . To offset this surplus work a quantity of heat is transferred from a higher temperature  $T_2$  to a lower one  $T_1$ . This work represents the maximum work obtainable because the cycle is reversible.

The total work,  $w$ , is as follows:

$$w = w_{AB} + w_{BC} + w_{CD} + w_{DA} = RT_2 \ln v_B/v_A + C_v(T_2 - T_1) + RT_1 \ln v_D/v_C + (-C_v[T_2 - T_1])^* \quad [7]$$

$$w = RT_2 \ln v_B/v_A + RT_1 \ln v_D/v_C = RT_2 \ln v_B/v_A - RT_1 \ln v_C/v_D \quad [8]$$

In order to obtain a further simplification the last equations of steps 2 and 4 are compared;

$$\frac{C_v}{R} \ln \frac{T_1}{T_2} = -\ln \frac{v_C}{v_B} \quad [9]$$

and

$$\frac{C_v}{R} \ln \frac{T_2}{T_1} = -\ln \frac{v_A}{v_D} \quad [10]$$

or

$$\frac{C_v}{R} \ln \frac{T_1}{T_2} = -\ln \frac{v_D}{v_A} \quad [11]$$

Obviously

$$\frac{v_C}{v_B} = \frac{v_D}{v_A} \quad [12]$$

and rearranging

$$\frac{v_C}{v_D} = \frac{v_B}{v_A} \quad [13]$$

and substituting equation (13) into equation (8)

$$w = RT_2 \ln \frac{v_B}{v_A} - RT_1 \ln \frac{v_B}{v_A} \quad [14]$$

Dividing this equation by  $q_{AB} = RT_2 \ln v_B/v_A$ , as given in the first step

$$\frac{w}{q_{AB}} = \frac{R(T_2 - T_1) \ln \frac{v_B}{v_A}}{RT_2 \ln \frac{v_B}{v_A}} = \frac{T_2 - T_1}{T_2} \quad [15]$$

\* It will be noted that all the work terms are *added* and that the relative magnitudes of the final and initial states determine the sign.



Writing  $q_2$  instead of  $q_{AB}$  for the heat absorbed at the higher temperature  $T_2$ , and remembering that the work is maximum work because the cycle is reversible,

$$w_{\max} = q_2 \frac{T_2 - T_1}{T_2} \quad [16]$$

This is the same as equation (40) on page 142 derived in a more general way.

### Specific Diffusion Rate\*

(Page 238)

$$D = \frac{RT}{N} \frac{1}{f}$$

where  $f$  is the frictional force opposing particles which move with a velocity of 1 cm. per sec., and  $D$  is the specific diffusion reaction rate.

The velocity  $v$  of motion of a molecule under the influence of a force  $K$  is

$$v = \frac{K}{f} \quad [1]$$

where  $f$  is the frictional resistance to the motion. If the concentration of the solution before a plane across which diffusion is taking place is  $c$  gram molecules per unit volume,  $cN$  molecules will be involved, with force  $K$  acting upon them, and

$$v = \frac{1}{cN} \frac{K}{f} \quad [2]$$

In diffusion the force acting is equal to the osmotic pressure gradient, therefore

$$K = - \frac{dP}{dx} = -RT \frac{dc}{dx} \quad [3]$$

and, by substitution and rearrangement,

$$- \frac{vc}{dc/dx} = + \frac{RT}{N} \times \frac{1}{f} \quad [4]$$

But the diffusion constant  $D$  is, by definition, the amount of solute which will diffuse in unit time, across unit area, under unit gradient of concentration; therefore

$$-D \frac{dc}{dx} = vc \quad [5]$$

It follows immediately that

$$D = \frac{RT}{N} \times \frac{1}{f} \quad [6]$$

### The Rate Equation

(Equation 43, page 374)

Eyring's equation for the activated complex is

$$k = \frac{RT}{Nh} e^{\Delta S_a/R} e^{-\Delta F_a/RT} \quad [1]$$

\* Einstein, *Z. Elektrochem.*, **14**, 235 (1908).

The concentration of the activated molecules is given in terms of an equilibrium constant  $K_a$  and the concentration of the reacting molecules, thus

$$\begin{aligned} c_{\text{activated molecules}} &= K_a c_{\text{reactants}} \sqrt{\frac{2\pi MRT}{N^2 h^2}} l \\ &= e^{-\Delta F_a/RT} \left( \sqrt{\frac{2\pi MRT}{N^2 h^2}} l \right) c_{\text{reactants}} \end{aligned} \quad [2]$$

where the term under the square root sign allows for the fact that in addition to the three translational degrees of freedom there is an extra degree of freedom along which the activated molecule is decomposing.  $N$  is the Avogadro number,  $h$  is Planck's constant, and  $l$  is a measure of the width of the activated state on the energy surface. The activated molecules are moving along the top of the energy barrier with a velocity  $\sqrt{\frac{RT}{2\pi M}}$  so that the length of time spent in the activated state is  $\frac{l}{\sqrt{\frac{RT}{2\pi M}}}$

Then the rate of the reaction is given by the expression

$$\text{Rate} = \frac{\text{Number of molecules in activated state}}{\text{Average time spent in activated state}} = \frac{e^{-\Delta F_a/RT} \left( \sqrt{\frac{2\pi MRT}{N^2 h^2}} l \right) c_{\text{reactant}}}{l / \sqrt{\frac{RT}{2\pi M}}} \quad [3]$$

$$\text{Rate} = \frac{RT}{Nh} e^{-\Delta F_a/RT} c_{\text{reactants}} \quad [4]$$

and

$$k = \kappa \frac{RT}{Nh} e^{\Delta S_a/R} e^{-\Delta H_a/RT} \quad [5]$$

The term  $\kappa$  is included to allow for the probability that a molecule once fully activated will give the products of the reaction. Ordinarily it is assumed that this probability is practically unity and  $\kappa$  is neglected.

### Debye-Hückel Theory

(Page 504)

Surrounding any ion in a solution there will be on the average a greater number of ions of opposite charge than of like charge, as a result of the attraction of unlike charges and repulsion of like charges. For a uni-univalent electrolyte, the number of positive ions,  $dn_+$ , or of negative ions,  $dn_-$ , in a volume  $dV$  at a distance  $r$  from a particular ion will be, according to the Boltzmann distribution law,

$$dn_+ = n e^{-e\psi/kT} dV \quad [1]$$

$$dn_- = n e^{+e\psi/kT} dV \quad [2]$$

Here  $n$  is the total number of positive or negative ions divided by the total volume,  $k$  is the Boltzmann constant, and  $e$  is the charge on a univalent positive ion.  $\psi$  is the electric potential or the work required to bring a unit positive charge from infinity to a distance  $r$  from the selected ion. The number of ions in the volume  $dV$  will of course fluctuate as the ions move about in the solution, but the equations hold for the values averaged over a period of time.

The density of charge  $\rho$  will be

$$\rho = \frac{(dn_+ - dn_-)\epsilon}{dV} = n\epsilon(e^{-e\psi/kT} - e^{e\psi/kT}) \quad [3]$$

Expanding the exponential terms into a series and neglecting higher terms, we have as a close approximation for small potentials

$$\rho = -\frac{2n\epsilon^2\psi}{kT} \quad [4]$$

The Poisson equation, derived from Coulomb's law, also relates  $\psi$  and  $\rho$ . Since  $\psi$  depends only on  $r$ , the equation is

$$\frac{d^2\psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr} = \frac{-4\pi\rho}{D} \quad [5]$$

In this equation,  $D$  is the dielectric constant of the medium. Substituting (4) into (5), we have

$$\frac{d^2\psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr} = \frac{8\pi n\epsilon^2\psi}{DkT} = \kappa^2\psi \quad [6]$$

where

$$\kappa^2 = \frac{8\pi n\epsilon^2}{DkT} \quad [7]$$

It can be verified that a solution of equation (6) is given by

$$\psi = A \frac{e^{-\kappa r}}{r} + B \frac{e^{\kappa r}}{r} \quad [8]$$

and since there are two independent arbitrary constants,  $A$  and  $B$ , this must be a general solution. The potential must approach zero as the distance  $r$  from the selected ion becomes very large, and so  $B$  must be zero; otherwise the term  $e^{\kappa r}/r$  will make  $\psi$  very large at large values of  $r$ .

$A$  can be evaluated by making use of the fact that the total charge surrounding the ion (which we will assume to be positive) must be  $-\epsilon$ , since the solution as a whole is neutral. Comparison of (5) and (6) shows that

$$\rho = -\frac{D\kappa^2\psi}{4\pi} = -\frac{D\kappa^2 A e^{-\kappa r}}{4\pi r} \quad [9]$$

Hence, integrating (by parts) from the closest distance of approach of the ions, which we will call  $a$ ,

$$\begin{aligned} -\epsilon &= \int_a^\infty 4\pi r^2 \rho dr \\ &= -\int_a^\infty r D \kappa^2 A e^{-\kappa r} dr \\ &= -DA e^{-\kappa a} (1 + \kappa a) \end{aligned} \quad [10]$$

Therefore

$$A = \frac{\epsilon e^{\kappa a}}{D(1 + \kappa a)} \quad [11]$$

and

$$\psi = \frac{e e^{\kappa(a-r)}}{D(1 + \kappa a)r} \quad [12]$$

The potential at the ion is the value of  $\psi$  at  $r = a$ ,

$$\psi = \frac{e}{D(1 + \kappa a)a} \quad [13]$$

In calculating the activity coefficients and other properties of the solution, Debye attributed all the deviation from the behavior of ideal solutions to the electric charges on the ions. Consider the following imaginary process.\*

1. Gradually discharge an ion in an extremely dilute solution of the electrolyte.
2. Transfer the discharged ion to a more concentrated solution.
3. Gradually charge the ion again.

The changes in free energy in steps 1 and 3 are equal to the electrical work done on the system, and the free energy change in step 2 is the same as for ideal solutions.

$$\begin{aligned} \Delta F_1 &= \int_{q=e}^{q=0} \psi dq = \int_{q=e}^{q=0} \frac{q}{D(1 + \kappa a)a} dq \\ &= -\frac{e^2}{2Da} \quad (\kappa \cong 0 \text{ here}) \end{aligned}$$

$$\Delta F_2 = \frac{RT}{N} \ln \frac{c}{c_0} = kT \ln \frac{c}{c_0}$$

where  $c$  and  $c_0$  are the concentrations of the final and initial solutions, respectively.

$$\begin{aligned} \Delta F_3 &= \int_{q=0}^{q=e} \frac{q}{D(1 + \kappa a)a} dq = \frac{e^2 \kappa}{2D(1 + \kappa a)a} \\ &= \frac{e^2}{2Da} - \frac{e^2 \kappa}{2D(1 + \kappa a)} \end{aligned}$$

Therefore

$$\Delta F = \Delta F_1 + \Delta F_2 + \Delta F_3 = kT \ln \frac{c}{c_0} - \frac{e^2 \kappa}{2D(1 + \kappa a)} \quad [14]$$

The free energy change is also given by the equation

$$\Delta F = \frac{RT}{N} \ln \frac{\gamma c}{c_0} = kT \ln \frac{c}{c_0} + kT \ln \gamma \quad [15]$$

where  $\gamma$  is the activity coefficient of the ion in the final solution.  $\gamma = 1$  in the initial solution.

Comparing equations (14) and (15), we see that

$$kT \ln \gamma = -\frac{e^2 \kappa}{2D(1 + \kappa a)} \quad [16]$$

Using equation (7) and  $n = c/1000N$ , where  $c$  is the concentration in moles per liter and  $N$  is the Avogadro number, equation (16) may be written as

$$\log \gamma = -\frac{e^2 \sqrt{8\pi c e^2 / 1000 N D k T}}{2.303 \times 2 D k T (1 + a \sqrt{8\pi c e^2 / 1000 N D k T})} \quad [17]$$

\* Guntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

If  $c$  is small, (17) becomes

$$\log \gamma = -A\sqrt{c} \quad [18]$$

where

$$A = \frac{\epsilon^2(2\pi)^{1/2}}{2.303(DkT)^{3/2}(1000N)^{1/2}} \quad [19]$$

This equation was derived for a uni-univalent electrolyte. The expression for the activity coefficient of other types of electrolytes in solutions containing different electrolytes (page 462) can be derived in a similar manner.

For water at 25°  $A = 0.503$ .

### Bohr's Formula for the Energy of an Electron in an Elliptical Orbit

(Page 555)

$$E_n = -\frac{2\pi^2m(Ze)^2e^2}{n^2h^2}$$

It is assumed that a negative electron moves in a circular orbit around a central nucleus which has a positive charge  $Ze$ , where  $Z$  is the atomic number and  $e$  is the unit electrical charge, i.e., the charge of an electron or proton.

The centrifugal force of the electron moving in its orbit is  $\frac{mv^2}{r}$ , where  $m$  is the mass of the electron,  $v$  is the velocity, and  $r$  is the radius of the orbit, i.e., the distance between the electron and the nucleus.

The electrical force of attraction is  $\frac{(Ze)e}{r^2}$  as given by Coulomb's law.

In the stable orbit the centrifugal force must be equal and opposite to the electrical force in order to maintain equilibrium.

Then

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad [1]$$

The total energy  $E$  is equal to the sum of the kinetic energy  $E_k$  and the potential energy  $E_p$ .

$$E_k = \frac{1}{2}mv^2 = \frac{1}{2}\frac{Ze^2}{r} \quad [2]$$

and

$$E_p = \int_{\infty}^r \frac{Ze^2}{r^2} dr = -\frac{Ze^2}{r} \quad [3]$$

Then

$$E = E_k + E_p = \frac{1}{2}\frac{Ze^2}{r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r} \quad [4]$$

The energy has a negative sign because the reference state with zero energy is taken as that state in which the electron is at infinite distance from the nucleus and the lower limit of integration is taken as  $r = \infty$ .

These considerations apply to any coulombic field and can be applied to elliptical orbits as well as to circular orbits.

The angular momentum  $p$  of the moving electron is given by the expression

$$p = mvr \quad [5]$$

Then substituting equations (5) and (1) into (4)

$$E = -\frac{Ze^2}{2r} = -\frac{Ze^2mv}{2p} = -\frac{Ze^2}{2p} \frac{Ze^2}{rv} = -\frac{Ze^2}{2p} \frac{Ze^2m}{p} = -\frac{mZ^2e^4}{2p^2} \quad [6]$$

If this formula were strictly correct  $E$  would change continuously over a wide range and a continuous spectrum containing all wavelengths would be produced. To account for the discontinuous spectrum which is actually produced Bohr assumed that the angular momentum of the electron in its orbit must be an integral multiple of  $\frac{h}{2\pi}$ , where  $h$  is Planck's universal constant. In other words, he assumed that the only values of  $p$  which are permitted by the restrictions of the quantum theory are those which meet the requirement of the equation

$$2\pi p = nh \quad \text{or} \quad p = \frac{nh}{2\pi} \quad [7]$$

where  $n$  is an integer 1, 2, 3, 4, etc.

Substituting into equation (6)

$$E_n = -\frac{mZ^2e^4(2\pi)^2}{2(nh)^2} = -\frac{2\pi^2mZ^2e^4}{n^2h^2} \quad [8]$$

#### SYMBOLS USED FOR THE MORE COMMON ABBREVIATIONS

$A$ work content	$\bar{V}$ partial molal volume
$\text{\AA}$ Ångström unit	$a$ activity
$C$ molar heat capacity	$c$ concentration; heat capacity
$E$ internal energy; activation energy	$d$ density
$E$ voltage	$e$ electron; electronic charge
emf. electromotive force	$h$ Planck's constant
$F$ free energy	$k$ specific reaction rate; gas constant per molecule
$\Delta F$ change in free energy	$m$ molality
$\Delta F^0$ change in free energy (standard state)	$n$ number of moles; refractive index
$F$ faraday (96,501 coulombs)	$p$ pressure
$H$ heat content	$pH$ measure of hydrogen-ion activity; $-\log a_{H^+}$
$I$ intensity of light	$q$ heat absorbed
$K$ equilibrium constant; absolute temperature scale	$t$ centigrade temperature; time
$K_b$ boiling-point constant	$v$ volume
$K_f$ freezing-point constant	$w$ work done
$L$ heat of vaporization; specific conductance	$\alpha$ angle of optical rotation
$M$ molecular weight; molarity	$\gamma$ activity coefficient; surface tension
$N$ Avogadro number; mole fraction	$\epsilon$ quantum
$P$ osmotic pressure	$\eta$ viscosity
$R$ gas constant	$\Lambda$ equivalent conductance
$R$ Rydberg constant	$\lambda$ wavelength of radiation
$S$ entropy	$\mu$ micron; dipole moment
$T$ absolute temperature	$\nu$ frequency of radiation
$V$ volume of 1 mole of gas	$\bar{\nu}$ wave number
	$\Phi$ quantum yield

# INTERNATIONAL ATOMIC WEIGHTS

1941

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	Sym- bol	Atomic Number	Atomic Weight		Sym- bol	Atomic Number	Atomic Weight
Aluminum...	Al	13	26.97	Molybdenum..	Mo	42	95.95
Antimony....	Sb	51	121.76	Neodymium..	Nd	60	144.27
Argon.....	A	18	39.944	Neon.....	Ne	10	20.183
Arsenic.....	As	33	74.91	Nickel.....	Ni	28	58.69
Barium.....	Ba	56	137.36	Nitrogen.....	N	7	14.008
Beryllium....	Be	4	9.02	Osmium.....	Os	76	190.2
Bismuth.....	Bi	83	209.00	Oxygen.....	O	8	16.0000
Boron.....	B	5	10.82	Palladium....	Pd	46	106.7
Bromine.....	Br	35	79.916	Phosphorus...	P	15	30.98
Cadmium.....	Cd	48	112.41	Platinum.....	Pt	73	195.23
Calcium.....	Ca	20	40.08	Potassium....	K	19	39.098
Carbon.....	C	6	12.010	Praseodymium..	Pr	59	140.92
Cerium.....	Ce	58	140.13	Protactinium..	Pa	91	231
Cesium.....	Cs	55	132.91	Radium.....	Ra	88	226.05
Chlorine.....	Cl	17	35.457	Radon.....	Rn	86	222
Chromium....	Cr	24	52.01	Rhenium.....	Re	75	186.31
Cobalt.....	Co	27	58.94	Rhodium.....	Rh	45	102.91
Columbium...	Cb	41	92.91	Rubidium....	Rb	37	85.48
Copper.....	Cu	29	63.57	Ruthenium...	Ru	44	101.7
Dysprosium..	Dy	66	162.46	Samarium.....	Sm	62	150.43
Erbium.....	Er	68	167.2	Scandium....	Sc	21	45.10
Europium....	Eu	63	152.0	Selenium.....	Se	34	78.96
Fluorine....	F	9	19.00	Silicon.....	Si	14	28.06
Gadolinium..	Gd	64	156.9	Silver.....	Ag	47	107.880
Gallium.....	Ga	31	69.72	Sodium.....	Na	11	22.997
Germanium..	Ge	32	72.60	Strontium....	Sr	38	87.63
Gold.....	Au	79	197.2	Sulfur.....	S	16	32.06
Hafnium.....	Hf	72	178.6	Tantalum....	Ta	73	180.88
Helium.....	He	2	4.003	Tellurium....	Te	52	127.61
Holmium....	Ho	67	164.94	Terbium.....	Tb	65	159.2
Hydrogen....	H	1	1.0080	Thallium....	Tl	81	204.39
Indium.....	In	49	114.76	Thorium.....	Th	90	232.12
Iodine.....	I	53	126.92	Thulium.....	Tm	69	169.4
Iridium.....	Ir	77	193.1	Tin.....	Sn	50	118.70
Iron.....	Fe	26	55.85	Titanium.....	Ti	22	47.90
Krypton.....	Kr	36	83.7	Tungsten....	W	74	183.92
Lanthanum..	La	57	138.92	Uranium.....	U	92	238.07
Lead.....	Pb	82	207.21	Vanadium....	V	23	50.95
Lithium.....	Li	3	6.940	Xenon.....	Xe	54	131.3
Lutecium....	Lu	71	174.99	Ytterbium....	Yb	70	173.04
Magnesium..	Mg	12	24.32	Yttrium.....	Y	39	88.92
Manganese...	Mn	25	54.93	Zinc.....	Zn	30	65.38
Mercury.....	Hg	80	200.61	Zirconium....	Zr	40	91.22

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# LOGARITHMS

Natural Numbers											PROPORTIONAL PARTS								
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	6	7	8	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

# LOGARITHMS

Natural Numbers	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	6	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4	4

# LOGARITHMS

Natural Numbers	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	6	7	8	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

# LOGARITHMS

Natural Numbers	0	1	2	3	4	5	6	7	8	9	PROPORTIONAL PARTS								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4	4